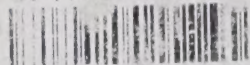


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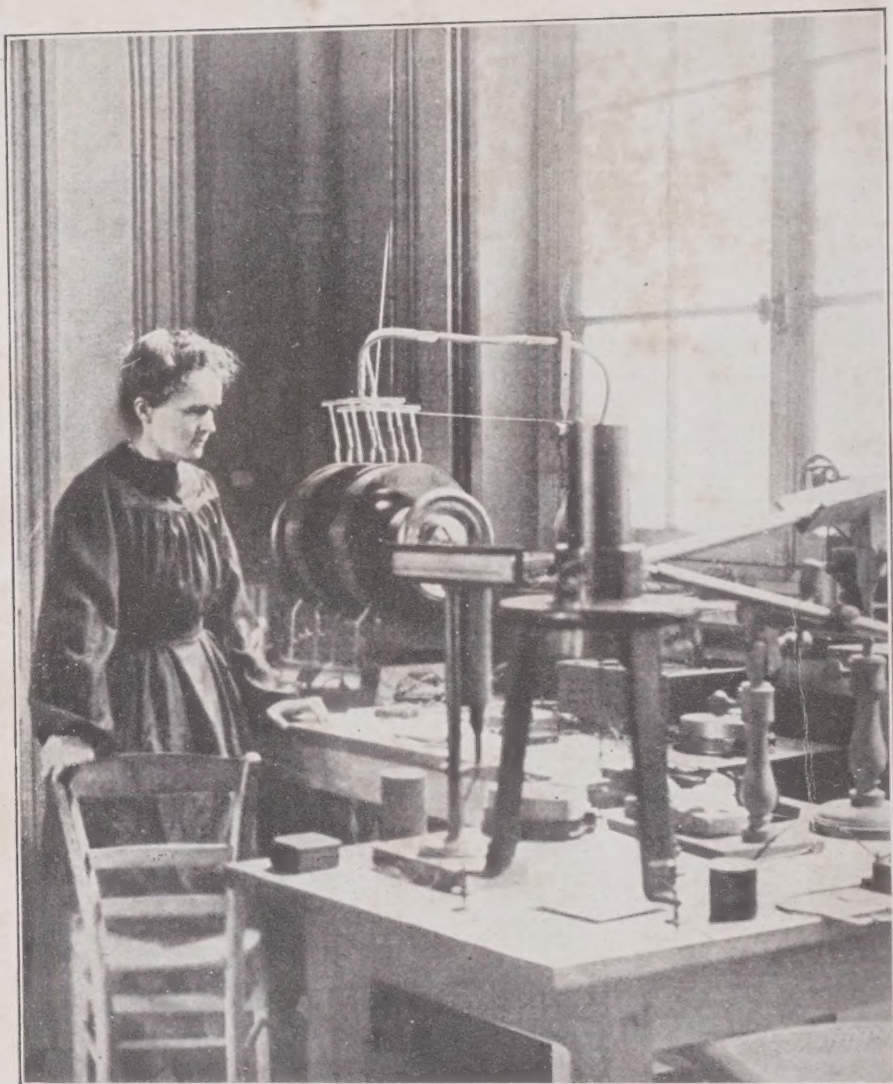


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INTRODUCTORY CHEMISTRY
WITH
HOUSEHOLD APPLICATIONS

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MADAME CURIE IN HER LABORATORY

Chemists, physicists, and physicians, as well as those in other fields of activity, know of the work of Madame Curie. A brief sketch of her studies of radioactive elements is given in Chapter XXVIII. An enumeration of her achievements is inadequate expression of our admiration of her. We have praised her; we have conferred degrees upon her; we have honored her with prizes and medals. Her life was one of intense devotion to research, and the results of her efforts are of inestimable value.

THE CENTURY CHEMISTRY SERIES

JAMES KENDALL, *Editor*

INTRODUCTORY CHEMISTRY

WITH HOUSEHOLD APPLICATIONS

BY

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Revised Edition



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PREFACE TO THE REVISED EDITION

In the revised edition, the authors have held to the original idea of providing an introductory chemistry text in which the illustrations are familiar to a girl from the experiences of her home. The aim is to build up the foundation principles of chemistry in such a way that the student of home economics will frequently encounter applications that will help her to understand the purpose of chemistry in her curriculum. It is hoped that, with this beginning, the home economics student will find for herself many more problems to solve in the intricate relationship between chemistry and the conveniences of the home.

The authors have extended the treatment of fundamental chemistry, as is indicated by the chapters on the quantitative reactions of acids and bases, the concepts of electrovalence, covalence, and coördinate valence, and the complete revision of the chapters on atomic structure and radioactivity. They have incorporated also some of the recent theory that has become firmly established through research; for example, the Debye-Hückel theory as applied to solutions of salts and to strong acids and bases. The student will find reference to many recent industrial applications of chemistry that are of interest in the field of home economics — synthetic textile fibers, glass fibers, synthetic plastics, and new alloys.

A list of suggestive readings has been prepared for each chapter; they are interesting references which, if studied, will extend the student's knowledge of current applications of chemistry. Wherever possible, references are confined to sources that are easily available.

The authors wish to acknowledge the help received from the faculty associates of their staffs and from many others who have contributed by their encouragement, suggestions, criticism, and advice. We are again indebted to Dr. J. A. Wilkinson of Iowa State College for a careful reading of the manuscript.

vi PREFACE TO THE REVISED EDITION

Criticisms and suggestions for improvement of the text will be welcomed by the authors.

NELLIE M. NAYLOR.

AMY M. LE VESCONTE.

PREFACE TO THE FIRST EDITION

Just at the opening of a college year, a group of prospective freshman girls were visiting the chemistry building of a certain college. They were shown the laboratories in which work was in progress on the analysis of textile fibers; they were shown a group of students in another laboratory making levulose, a sugar which can be used by diabetics; in still another laboratory a medicinal compound to allay pain was being made. With each glimpse of these interesting activities the prospective freshmen became more astonished. "Is that what chemistry is about?" they inquired. The girls' inquiry was answered by their guide with the explanation that chemistry is concerned with materials of daily importance to all of us.

The authors of this textbook believe that chemistry should appeal to the interest and imagination of the home economics student. They know very well the difficulties involved in planning a middle course between making a subject too practical and making it too theoretical. Realizing that home economics curricula include advanced courses in chemistry and foundation work in bacteriology, zoölogy, and other sciences, they have chosen the subject-matter of this text so as to give a knowledge of the principles of chemistry required for later courses. However, these principles may be studied in their relation to the field of home economics. Wherever possible, illustrations are chosen that are familiar to any girl from her home life. It is hoped that this chemistry text may appeal to the home economics student not because its subject-matter is unusual, but because an attempt has been made throughout the text to present suggestions that may help the reader to sense the relationship between chemistry and home economics.

Since current literature and lectures involve discussions of protons and electrons, it is evident that the teacher of chemistry must not overlook modern theories and discoveries. Throughout

the text, chemistry is presented as a growing subject in which new knowledge is constantly being acquired by research. To follow through the development of some principle of chemistry and to make application of it to problems of current interest is to think in terms of chemistry. It is with this in mind that the authors have introduced the student to practical home economics problems by such chapters as "Leavening Agents," "Water and Its Uses," "Chemistry in the Laundry," and "The Colloidal State."

Material for the text has been gleaned from textbooks of home economics and chemistry too numerous to list. Articles from the *Journal of Chemical Education* and other scientific publications have furnished suggestions. The authors take this opportunity to acknowledge the help obtained from these sources.

When a teacher suggests a task, the student generally meets the challenge. A suggestion made by Professor James Kendall to one of the authors resulted in the writing of this book. We are indebted to Professor Kendall, the editor of the Century Chemistry Series, for his encouragement and advice. We are especially grateful to Dr. J. A. Wilkinson of Iowa State College for the many helpful suggestions which resulted from his careful reading of the manuscript. Certain chapters were read and criticized by Dr. R. A. Gortner of the University of Minnesota, Dr. F. E. Brown, Dr. Rachel Edgar, Professor John Buchanan, Professor Belle Lowe, and Mrs. Florence W. Nichols of Iowa State College, Dr. Harold Maxwell of E. I. DuPont de Nemours & Company, and T. J. Bryan of Chicago. To these the authors express their appreciation. Many assistants in the department of chemistry at Iowa State College, as well as Miss Ruth Gerber of Oklahoma Agricultural and Mechanical College, have offered valuable suggestions and pointed out errors in the manuscript as they have used it in their class work.

Credit for photographs is given in the text. The diagrams were prepared by Mrs. Marian Weston Van Ess, Miss Irene Conlee, and Mr. John Murphy. Suggestions and criticisms of the text will always be welcomed by the authors.

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INTRODUCTORY CHEMISTRY
WITH
HOUSEHOLD APPLICATIONS

CHAPTER I

THE LANGUAGE OF CHEMISTRY

Introduction. — When first the subject of chemistry is approached by students of home economics or, indeed, of any other curriculum, questions immediately arise as to the purpose it fulfils in their chosen field. Why is chemistry a required course in many curricula? Why do many people claim that an education is incomplete without some knowledge of chemistry?

These questions may be partially answered by saying that chemistry teaches us about the composition of the materials that we use every day and helps us to understand what happens when certain changes take place in these materials. We cannot in a few words give the scope of chemistry. It is sufficient for the present to realize that the study of chemistry will enable us to know more about the matter around us and to understand how we happen to possess some of the simple conveniences of life.

Chemistry may be defined as the science that treats of matter and its changes. Some of the kinds of matter that will be studied in chemistry are water, air, copper, iron, brass, ammonia, washing soda, baking soda, sugar, aluminium, sand, lime, salt, and borax. We shall learn about many changes that these substances undergo, such as the tarnishing of copper, the burning of wood, the decomposition of sugar, and the reaction of baking soda with sour milk.

Many substances that are in everyday use in the home do not occur in nature in a form familiar to us. Chemical methods are employed to manufacture certain products or to obtain them by purification of natural materials. A few examples will help to show the value of chemistry in this important field of work. Aluminium occurs in nature principally in the form of clay, while iron occurs as iron rust. The chemist must devise a way to obtain the metals from their natural sources. Again, we are in debt to the chemist

for the many kinds of dyes commonly used in the home. In early times the only dyes available were those obtained from plant juices or from some other natural source. Gray, drab, brown, indigo blue, and cochineal red were some of the few colors that could be obtained. What a contrast to the brightly colored and fadeless dyes that we now enjoy! It was the chemist who, by accident, discovered that a dye could be made from sticky coal-tar. Since the time of this discovery, coal-tar dyes have been developed until we have an almost limitless variety of stable colorings for our clothing and for home decoration. Again, a more recent development, well known to some of us, is the manufacture of silky textiles from commonplace material. Through chemical processes it has been possible to make very attractive and durable fabrics from the cellulose of cotton, wood, corn-stalks, and other inexpensive substances. More recently, textiles have been produced from synthetic fiber-forming compounds of a protein-like structure. One of these fibers, made from coal, air, and water, has the elasticity necessary for use in hose. Other textiles are made of glass fibers, of rubber fibers, and of a wool-like fiber made from casein. Besides the synthetic dyes and the new textiles, the chemist has devised sizings, waterproofings, and dressings to improve the older textiles and to make them adaptable for a variety of uses.

Chemistry presents a field of especial interest to women, for in every part of the home we find convenient articles that have been made through chemical research. Only a few can be mentioned, such as our dishes and silver ware, pewter, stainless steel, enameled ware, and colored or frosted glass tumblers, all of which are gifts resulting from processes of chemistry. Plastics have been made from casein, from urea, and from cellulose that make so many durable and interesting colored articles — knife handles, umbrella handles, trays, salt and pepper shakers. For laundry work, chemistry has given us soaps that are effective in hard water, washing powders, bluing, water softeners, and stain-removing reagents.

The preparation and use of foods involves many problems which the chemist is called upon to solve. Chemists have studied foods

to determine their composition and vitamin content. They have learned the nature of vitamins and of other food accessories and have learned the influence of these substances on general health and nutrition. This information is of great help in meal-planning; it enables us to use pleasing and attractive foods in diets that contain all the substances essential to nutrition. Food preservation also is the work of the chemist, as well as the preparation of many convenient and necessary products such as evaporated milk, baking powder, flavorings, cheese, and breakfast foods.

Again we are indebted to chemistry when we realize the many discoveries that have helped the physician to do his work. Familiar to many readers are the anesthetics, such as ethylene, novocaine, ether, chloroform; and the disinfectants, such as chlorine, iodine, and mercurochrome. These have contributed in a large measure to make surgery safer and less painful. In addition to these useful substances, we have important preparations such as thyroxin, adrenaline, sulphanilamide, aspirin, and digitalis with which to allay suffering and conquer disease.

New words and terms and sometimes new meanings of familiar words must be learned in order to read and understand chemistry. Much confusion would be avoided if, at the beginning, the student learned to use correctly certain technical words important in the study of chemistry. A few of the typical terms and their applications are included in the following paragraphs. However, it must be kept in mind that the task of learning the language of chemistry is not finished with the mastery of these few terms.

Matter. — The science of chemistry treats of matter and its changes in energy and in composition. *Matter* is considered to be any substance that occupies space or that has mass. It may be a solid such as wood, a liquid such as water, or a gas such as air. Although it is quite evident that wood and water occupy space and have mass, it may be more difficult to think of air as having these properties. However, we realize that air occupies space when we attempt to pour water into a narrow-necked bottle in which there is no other opening through which the air may es-

cape. That air has mass may be deduced from the slight but appreciable difference in the weight of an exhausted vessel and of the same vessel filled with air.

Energy. — *Energy* is considered to mean the ability to do work. Heat, light, and electricity bring to mind familiar forms of energy. Many evidences of chemical energy are around us, but we are not so familiar with the term. **Chemical energy** is that energy possessed by certain substances which enables them to undergo chemical change. When coal burns, its chemical energy is changed into other forms of energy, such as heat and light. We may consider the reverse change in matter in which heat and light are absorbed and transformed into chemical energy. For instance, this process takes place in nature when the green leaves of plants in the presence of sunlight change substances found in the air and soil into plant material. Chemical energy, then, is stored in these plant materials until it may be released in some other form of energy when the plant is burned or used as food. If we should state these changes from the standpoint of matter, it would be to say that coal, which is carbon, burns in oxygen of the air, forming carbon dioxide, and in the chemical change releases its chemical energy in the form of heat and light.

Units of Measurement. — Before changes in matter and energy could be studied efficiently it was necessary that scientists have definite standards of measurement in order that results obtained by different workers might be compared. It is advantageous to have these units based on a decimal system, since this facilitates calculations; this advantage may be seen readily when comparison is made of the ease with which we calculate in dollars and cents and the difficulty that we find in using measurements such as rods, yards, feet, and inches.

The English system of measurements, also used in American commerce, is based on the proportions that were at one time convenient but not necessarily accurate, such as feet and finger breadths. The English have since fixed by law a definite length, marked on a special bronze bar, as a standard yard. They have

used this unit to define other lengths such as feet and inches, and have adopted certain relationships between length and volume, for example, the number of cubic inches per gallon. However, as we know, the ratios between these units are arbitrary and have no scientific basis. At the time of the French Revolution, scientists in Paris devised a more scientific system of measurements based on a decimal system. Because of the ease with which calculations can be made in this system, because it is in general use in Continental Europe, and because it is known all over the world, scientists use it exclusively. Most of them hope that before many years this system will be familiar enough to the residents of the United States so that it may be adopted as the standard in all commercial transactions.

In the metric system, the standard **unit of length** is the **meter**. This length, a little longer than a yard, is marked on three platinum-iridium bars. These are reference standards and one of them is kept at each of the cities — Paris, London, and Washington. Decimal divisions of the meter are millimeters, centimeters, and decimeters. The following table shows the relationship of these units:

10 millimeters (mm.)	= 1 centimeter (cm.)
10 centimeters	= 1 decimeter (dm.)
10 decimeters	= 1 meter (m.)
1,000 meters	= 1 kilometer

The **volume unit** in the metric system is the cubic centimeter (c.c.), the volume of a cube 1 cm. \times 1 cm. \times 1 cm. A larger volume, the **liter**, contains 1,000 cubic centimeters. In the laboratory, volumes of liquids are measured with graduated cylinders similar to the measuring cups used in cooking. They are marked to read in cubic centimeters and are made to measure volumes from a few cubic centimeters to three liters or larger.

The **unit of weight**, the **gram**, was determined as the weight of one cubic centimeter of water at the temperature of its greatest density.¹ Decimal divisions of the gram are milligrams, centi-

¹ A slight change has been made in the length of the standard meter, which has necessitated a corresponding change in the other units of length. Because

grams, and decigrams. The following table shows the relationship of these units:

10 milligrams (mg.)	= 1 centigram (cg.)
10 centigrams	= 1 decigram (dg.)
10 decigrams	= 1 gram (g.)
1,000 grams	= 1 kilogram

The relationship between the units of the metric system and those of the English system is given in Table I (see also Appendix, Section 1).

TABLE I

RELATIONSHIP BETWEEN SOME FAMILIAR UNITS OF MEASURE AND THE
CONSTANTS OF THE METRIC SYSTEM

1 centimeter (0.01 m.)	= 0.03937 in.
1 meter (100 cm.)	= 39.37 in.
1 liter (1,000 c.c.)	= 1.057 qt.
1 cubic centimeter (0.001 l.)	= 0.2 teaspoon
1 kilogram (1,000 g.)	= 2.2 lb.
1 inch	= 2.54 cm. (0.0254 m.)
1 quart	= 946 c.c. (0.946 l.)
1 cup	= 237 c.c. (0.237 l.)
1 tablespoon	= 15 c.c. (0.015 l.)
1 pound	= 453.6 g. (0.4536 kg.)

Temperature measurements also have been placed on a decimal basis. On the original Fahrenheit scale, which is still in general use in this country, the freezing-point of water was arbitrarily marked as 32° F. and the boiling-point of water as 212° F., with other divisions made according to the same scale. In order to have a temperature scale to correspond with the metric system, the centigrade scale was devised. On it the freezing-point of water is

the value of the unit of weight was not made to correspond with the unit of length, the standard gram is the weight of 1.000027 cubic centimeters of water at the temperature of its greatest density. It follows that the liter, which is defined as the volume occupied by 1,000 grams of water at the temperature of its greatest density, is equal to 1,000.027 cubic centimeters. In accurate work the volume of a thousandth of a liter is designated as a **milliliter** to distinguish it from a cubic centimeter. Because the variation between the two volumes is so small, the term **cubic centimeter** will be used to designate the volume of a cube that measures one centimeter on each edge and likewise to designate the volume of one thousandth of a liter.

taken as 0°C . and the boiling-point of water as 100°C . This is the scale used in science to-day. It is evident that a kettle of water at 100°C . represents a greater quantity of heat than a cup of water at the same temperature. Experiments have shown that boiling water can radiate nine times as much heat as the same weight of iron at the same temperature. These examples show the necessity of being able to measure and to express the quantity of heat in a substance as well as its temperature. The unit of heat quantity — the **calorie** — is the amount of heat required to raise the temperature of one gram of water through one degree centigrade.² Larger quantities of heat are expressed as large calories, or **Calories**, equal to 1,000 small calories.

In some changes studied in chemistry, such as the burning of coal or the oxidation of food in the body, we are more interested in the quantity of heat energy that may be derived from such chemical reactions than in the actual changes in composition that take place. This heat of reaction may be determined experimentally by the use of a bomb calorimeter as shown in Figure 1. A definite weight of food is placed in the small platinum vessel B. This container is held inside of a water-tight compartment (or bomb) filled with oxygen under pressure. A fine iron wire passes through the food and is attached at C and C' to a source of electric current. A momentary passage of the current ignites the iron wire, which in turn ignites the food in the vessel B. The burning of the food evolves heat which is to be measured. The vessel surrounding the bomb contains a known weight of water at a temperature (t_1) which can be measured by the thermometer. A paddle serves to stir the water so that all of it will be heated alike. The water surrounding the bomb eventually absorbs all the heat given out by the burning food and the final temperature (t_2) is recorded. By definition, a calorie is the amount of heat required to raise the temperature of one gram of

² The amount of heat required to raise the temperature of one gram of water through 1°C . is not quite the same at every temperature, and the average of the values between 1°C . and 100°C . is that obtained at from 15°C . to 16°C . Hence, the calorie is more correctly defined as the amount of heat required to raise the temperature of one gram of water from 15°C . to 16°C .

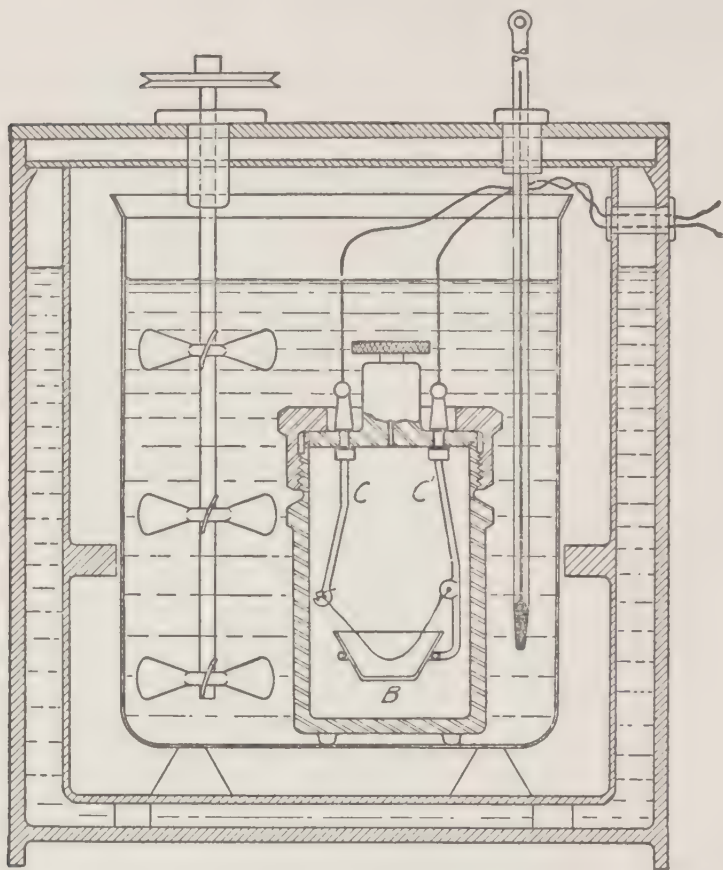


FIG. 1. Bomb Calorimeter

water through one degree centigrade. Therefore, the calories evolved by the burning of a gram of food may be determined by the following method:

$$\text{Cal.} = \frac{\text{weight of water} \times (t_2 - t_1)}{\text{weight of food}}$$

In the experimental work, it may be necessary to make some corrections. For example, a small amount of heat is given out by the burning of the iron wire. Also if the temperature of the water in the outside jacket changes, there is an indication of the radiation of some heat from the inner compartment. However, with

careful adjustment, the calorimeter is the best known device for determination of the calorific value of foods and of fuels. Tables are available giving the energy values of most of our well-known foods.

Properties of Matter. — The **properties** of a substance are the descriptive characteristics by which it may be identified. Certain physical properties, such as color, taste, odor, and physical state (solid, liquid, or gas), serve to help in identification. For complete identification it is customary to note also the chemical properties, such as ability of the substance to burn or combine with any other element or the ability to decompose or to retain its identity when acted upon by heat or some force. As an illustration of the properties of matter, we are enumerating physical properties of metals when we say they are lustrous, malleable solids (excepting mercury, which is a liquid), and good conductors of heat and electricity. We are stating a chemical property of sulphur when we say that it burns or oxidizes in the air, and likewise of sugar when we say that it may, by heat, be decomposed into carbon and water. In the laboratory a good chemist is recognized by his ability to observe and remember the properties of substances studied, and especially to distinguish the properties that are important in differentiating between various substances.

Changes in Matter. — In the study of matter, two distinct types of changes will be encountered, namely, **physical** and **chemical changes**. Matter changes its physical state when steam, or ice, is formed from liquid water, or when solid glass melts to a red, pliable mass, or when moth-balls evaporate, changing from a solid to a gaseous condition. Comparing the properties of water with those of steam, those of rigid glass with those of molten glass, or those of a solid with those of a gaseous moth preventive, we note certain differences in physical characteristics in each case. However, there is not any change in the chemical composition of any of these substances. This means that water, steam, and ice are composed of the same elements, that the solid glass and the red, pliable glass are essen-

tially alike, and that the solid and the gaseous moth preventive have the same composition.

Other changes which take place around us are more complicated. They are concerned with a change in composition: sometimes a combination of elements into more complex substances, sometimes the decomposition of matter into simpler forms. These are chemical changes; there is a change in composition, in chemical energy, and in the physical and chemical properties of the substances involved. Chemical changes are taking place when plants form from seeds, grow, die, and decay; when milk sours; and when wood or coal burns in the fireplace.

In the laboratory, we may heat and burn a piece of magnesium ribbon to illustrate a chemical change. Magnesium possesses chemical energy which is changed to heat and light during the reaction; that is, a change in chemical energy is noted. The white powder formed by the combination of magnesium with oxygen is evidence of a change in composition; a new substance is formed with properties quite different from those of the elements entering into the reaction. The fact that magnesium and oxygen combine to form one substance may be expressed briefly and clearly in a form known as a chemical statement:



In summary, whenever a physical change takes place, there is a change in the physical properties of the substance, but the same kind of matter exists and may change back to its original form when removed from the influence of the force producing the change. *Whenever a chemical change takes place, there is a change in composition, in chemical energy, and in the properties of the substance.* The product obtained will not revert to the original substances except through another chemical change.

Laws and Theories. — Every science is based on an observation of facts followed by a correlation of these facts to form general principles or **laws**. Hence, in science, the word *law* means a statement describing some general fact or constant mode of behavior. A fundamental law of chemistry is the law of conservation of

matter, which may be stated as follows: *Whenever substances change in composition, the total weight of matter entering into the change is equal to the weight of matter in all of the products*; in other words, there is no gain or loss in weight during a chemical change. Thus when sugar is decomposed by heat (in the absence of air), the sum of weights of the carbon and water formed as products is exactly equal to the weight of sugar entering into the reaction. The truth of the law of conservation of matter will be demonstrated many times during this study.

Another important truth, known as the law of conservation of energy, may be stated thus: *There is no gain or loss in energy when it changes from one form to another*. For example, when coal burns, its chemical energy is not destroyed but is changed into heat energy. By means of a steam-engine heat energy may be transformed into energy of motion, called kinetic energy. The kinetic energy, in turn, may be transformed into electricity by a dynamo. In each change some energy is probably wasted, but the total quantity of energy obtained is the same as the chemical energy originally given up by the coal when it was burned.

Scientists are not satisfied with formulating laws concerning chemical facts: they must explain why such laws are true. These explanations are necessarily based partly on imagination, although they must be in harmony with all observed facts. When the explanations are first formulated and have not been tested to determine whether or not they are in harmony with all facts, they are called **hypotheses**. After several experiments have been made to test the accuracy of an hypothesis and scientists accept it as a plausible explanation of certain facts, it is known as a **theory**. Theories, in general, cannot be proved, but many of them are accepted as true because they correspond to all known facts. They are useful in prophesying the changes that may be expected under definite conditions. Since they are not as fully based on facts as are laws, they are more apt to be modified or discarded for more useful theories. This has been true since the first chemists began to wonder about the science as early as 500 B.C. It must be realized that chemistry is "not made but is in the making."

In this chapter, many important words have been defined and

some laws formulated. It is most necessary to study these carefully and to be able to use these words with their correct chemical significance. The following questions and problems will help to accomplish this.

QUESTIONS AND PROBLEMS

1. Explain the meaning of the terms *science, chemistry, matter, energy, properties of matter, meter, liter, gram, calorie, Calorie, chemical energy, cubic centimeter, milligram, kilogram.*
2. By using illustrations, distinguish between matter and energy; physical and chemical properties; chemical change and physical change; the English and the metric system of measurement; law and theory; Fahrenheit and centigrade thermometer scales.
3. Illustrate the law of conservation of energy by tracing the changes through which energy from the sun may pass and eventually be used to heat an electric toaster.
4. Give some properties which might serve to identify each of the following: sugar, salt, air, alcohol, sulphur.
5. Which is larger — a meter or a yard, a decimeter or 4 inches, an inch or a centimeter, a pint or 400 c.c., a kilogram or one-half pound?
6. A pencil is 12 cm. in length. Express its length in meters, in millimeters, and in inches.
7. A box measures 8 cm. \times 6 cm. \times 20 cm. Find its volume in cubic centimeters and in liters. What weight of water will it hold? What weight of mercury will it hold? (One c.c. of mercury weighs 13.6 grams.) What weight of air will it hold? (One liter of air weighs 1.29 grams.)
8. A textbook is 7 in. by $5\frac{1}{2}$ in. Express these dimensions in centimeters, millimeters, and meters. Express the area as square centimeters.
9. A box is 6 in. \times 8 in. \times 3 in. What are its dimensions expressed in centimeters? Find its volume in cubic centimeters, liters, and quarts.
10. How many liters in one gallon? What weight of alcohol will a gallon measure hold? (One c.c. of alcohol weighs 0.8 g.) What weight of air will it hold? (One liter of air weighs 1.29 g.)
11. A dress pattern requires $4\frac{3}{4}$ yds. The clerk in Paris would ask how many meters you want. What should be the answer?
12. Name some advantages of using the metric system of measurement.
13. A recipe for candy includes two cups of sugar, one-half cup of water, one-half pound of nuts, and one teaspoon of vanilla. Express these quantities in the metric system.
14. If 22 liters of a gas weigh 31.4 grams, what will one liter weigh? What will 400 c.c. of the gas weigh?

15. Find the weight of a liter of a certain gas from the fact that 600 c.c. of the gas weigh 1.2 grams.
16. Compare the cost of gasoline at 18¢ a gallon and 6¢ a liter.
17. Make a diagram of a calorimeter and explain its operation and its application to the determination of the energy values of foods.
18. How many calories will be required to raise the temperature of 60 g. of water from 15° C. to 90° C.?
19. How many calories of heat are required to raise the temperature of 112 grams of water from 20° C. to boiling temperature?
20. When burned in a calorimeter, 3.28 grams of food raise the temperature of 2,240 grams of water from 25° to 32° C. What is the calorific value per gram of food?
21. When 2 grams of bread are burned in a calorimeter holding 1,500 grams of water the temperature of the water is raised from 16° C. to 21° C. Find the number of Calories obtained from a gram of bread and find the number of grams of bread in a 100 Calorie portion.
22. Classify the following as physical or chemical changes: burning sugar, making syrup from sugar and water, action of soda and sour milk, freezing ice-cream, souring milk, melting ice, burning wood, boiling water, evaporation of moth-balls, burning magnesium.
23. When coal burns, the weight of the ashes left is much less than the weight of the original coal. Explain how this statement is consistent with the law of conservation of matter.
24. Complete the statements for the following chemical changes:

magnesium + oxygen →

iron + sulphur →

sugar (heated) →

carbon + oxygen →

copper + sulphur →

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Sci. Mo. — *Science Monthly*

Ind. Eng. Chem. — *Journal of Industrial and Engineering Chemistry*

Sci. Amer. — *Scientific American*

J. A. C. S. — *Journal of the American Chemistry Society*

Chem. Rev. — *Chemical Reviews*

Chem. and Met. Eng. — *Chemical and Metallurgical Engineering*

Phys. Rev. — *Physical Review*

J. Soc. Chem. Ind. — *Journal of the Society of Chemical Industry*

Chem. in Ind. — *Chemistry in Industry*

³ This list gives the full name of those magazines whose titles appear in abbreviated form in the references at the end of each chapter.

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CHAPTER II

FORMULAS AND EQUATIONS

Elements. — Matter as it occurs in nature is usually in the form of compounds and complex mixtures. Chemists, studying these various kinds of matter, have shown that many of the common materials of nature may be decomposed through chemical reactions, into smaller units of matter. Finally, there are obtained elementary substances which resist all further decomposition by

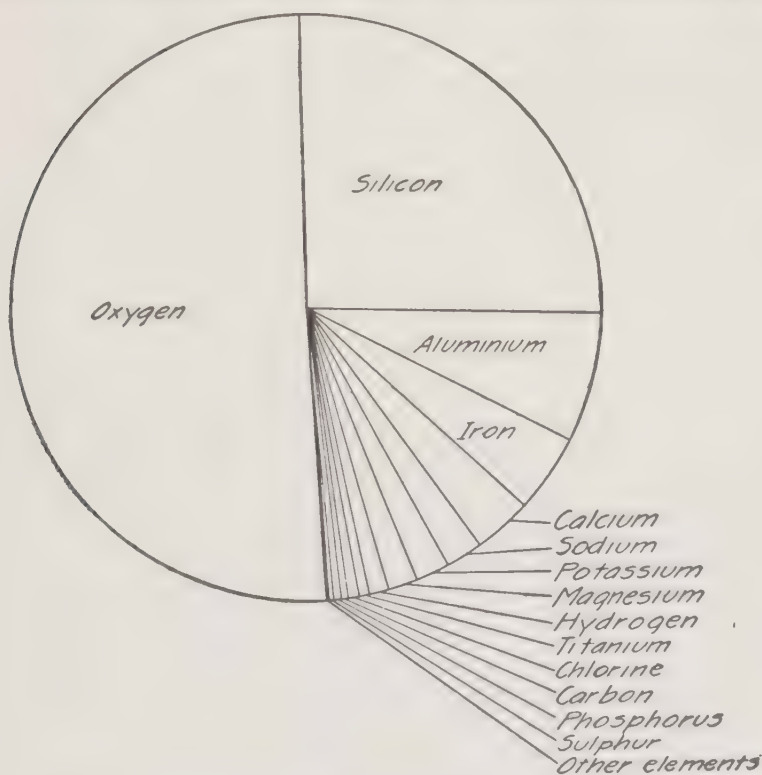


FIG. 2. Distribution of Elements in the Earth's Surface
(Including the Atmosphere)

INTRODUCTORY CHEMISTRY

TABLE II
AVERAGE COMPOSITION OF THE EARTH'S SURFACE,
INCLUDING THE ATMOSPHERE

(F. W. Clarke)

<i>Element</i>	<i>Per cent (weight)</i>
Oxygen	50.02
Silicon	25.80
Aluminium	7.30
Iron	4.18
Calcium	3.22
Magnesium	2.08
Sodium	2.36
Potassium	2.28
Hydrogen	0.95
Titanium	0.43
Carbon	0.18
Chlorine	0.20
Phosphorus	0.11
Sulphur	0.11
Barium	0.08
Manganese	0.08
Strontium	0.02
Nitrogen	0.03
Fluorine	0.10
Other elements	0.47

the usual chemical methods. Furthermore, these elementary substances have never been built up or synthesized from any kinds of matter that we now know. We use the word **element** to designate substances such as iron, oxygen, hydrogen, and carbon that, as explained in the foregoing, have never been decomposed into or made from any elementary units of matter. At present, ninety-two elements have been observed, and there is reason to believe that no others exist. Just as architects can use a few kinds of materials, such as bricks, wood, and cement to devise many kinds of buildings, so nature has used these ninety-two elements to make the infinite variety of substances, mineral and organic, found on the earth. Even the sun and stars have been shown to consist of none other than these same elements, either as such or in combination. There occur in nature a few elements such as

TABLE III
AVERAGE COMPOSITION OF THE HUMAN BODY
(H. C. Sherman)

<i>Element</i>	<i>Per cent (approximate)</i>
Oxygen	65.
Carbon	18.
Hydrogen	10.
Nitrogen	3.
Calcium	1.5
Phosphorus	1.0
Potassium	0.35
Sulphur	0.25
Sodium	0.15
Chlorine	0.15
Magnesium	0.05
Iron	0.004
Iodine	0.00004
Fluorine	{ very
Silicon	
Perhaps other elements	
	{ minute
	{ amounts

carbon (in the form of diamonds), gold, and sulphur. Air is a simple mixture of two gaseous elements, oxygen and nitrogen. Other elements, though abundant in nature, occur only in combination. Examples are chlorine in salt (sodium chloride), silicon in sand (silicon dioxide), and iron in iron ore (iron oxide).

A list of the ninety-two known elements is given in the appendix. It is interesting to know that, while many of them are found only in traces, over 50 per cent of the earth's surface consists of one element, oxygen. Table II shows the percentages of the more abundant elements that occur in the earth's surface, and Table III shows those that occur in the human body. The elements are often divided into two groups, the **metals**, such as tin, lead, zinc, copper, and gold, and the **non-metals**, such as oxygen, hydrogen, nitrogen, carbon, iodine, phosphorus, and sulphur. These two groups of elements are different in many respects and their distinguishing characteristics will be studied later.

Symbols. — In the earliest records of our science, chemists used symbols to represent elements. For example, \odot meant hydrogen,

and O meant oxygen. To-day, chemists have decided upon certain abbreviations of the names of the elements, which they call symbols. Thus, O represents oxygen, S represents sulphur, Zn represents zinc. The first letter of the name of the element is used as a symbol, unless there are two elements having the same initial letter. In that case, two letters are used. For example, C represents carbon, while Cl represents chlorine and Ca represents calcium. The symbols for some elements are derived from the common name in some other language, as Cu (cuprum) for copper, Ag (argentum) for silver, Hg (hydrargyrum) for mercury, Au (aurum) for gold, and Na (natrium) for sodium. A complete list of names of elements with their symbols is given on the back cover of the book. It will be necessary to learn the symbols for many of the common elements as we continue our study.

Compounds and Mixtures. — In the preceding pages, many compounds were mentioned, such as sugar, salt, water, chalk, and baking soda. It requires a study of the method of making a compound to determine how compounds differ from elements or mixtures. We may watch the lustrous metal, magnesium, burn in oxygen (a gaseous element) to form the compound magnesium oxide. It is a white, ash-like substance; that is, the properties are unlike those of magnesium and of oxygen. Magnesium oxide is made through a chemical change in which heat and light are evolved; and a definite proportion by weight of magnesium and of oxygen are present in every sample of pure magnesium oxide. As another illustration, we may compare the properties of sugar (a compound) with those of the elements present in sugar — carbon, hydrogen, and oxygen. Sugar is a white, crystalline solid, soluble in water, while carbon is a black solid and hydrogen and oxygen are colorless gases. It requires chemical changes to make sugar or to resolve it into the elements carbon, hydrogen, and oxygen. Also, accurate experiments have shown that carbon, hydrogen, and oxygen are present in the same weight ratio in every sample of pure sugar. From these examples, then, we may conclude that three characteristics are required to classify a substance as a **compound**: the properties of the compound are differ-

ent from those of the constituent elements; a chemical change is required to make compounds from elements or to decompose the compound into elements; and definite weights of matter enter into combination when a compound is made.

It is a simple matter to prepare a mixture of two or more elements, or a mixture of two or more compounds, or a mixture of



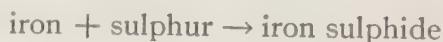
FIG. 3. Distribution of Elements in the Human Body

elements and compounds. Such mixtures as pepper and salt, sugar syrup, fruit juices, milk, baking powder and the air we breathe are most familiar. A study of the characteristics of a typical mixture such as sugar syrup shows that the properties of sugar in the syrup are essentially like those of dry sugar, that no chemical change or energy change is necessary in stirring sugar and water together and also no chemical change is involved when water evaporates to form dry sugar again, and that varying pro-

portions by weight of sugar and water may be used in making sugar syrups. It is evident, then, that the properties of a **mixture** correspond to those of the initial substances, that no energy change is involved in the preparation of a mixture, and that varying amounts of the constituent parts may be present in a mixture.

The distinction between a mixture and a compound is well illustrated by one of the laboratory experiments. Powdered iron and powdered sulphur are mixed intimately in a mortar. There is no change in chemical energy, and when the mixture is viewed through a microscope, the individual particles of sulphur and iron are easily distinguished. If a magnet is brought near the mixture, the iron particles are attracted. If the mixture is added to carbon disulphide, in which sulphur is soluble, the sulphur dissolves leaving the iron particles. These facts indicate that the sulphur and the iron have retained their characteristic properties in the mixture.

After a study of the properties of the mixture, chemical union of the constituent elements may be started by heating the mass. As the iron and sulphur combine, a red glow passes through the material. The heat and light evolved give evidence of chemical change. An examination of the resulting product will also show remarkable changes in properties. The magnet no longer attracts the iron, carbon disulphide no longer dissolves the sulphur, and when the powdered compound is studied under the microscope, a gray material called iron sulphide is seen, which resembles neither iron nor sulphur. The statement of the chemical change may be written:



In attempting to determine whether a substance that is not a pure element should be called a mixture or a compound, one may note whether it appears homogeneous under a microscope, whether the properties of the substance are different from those of the components, and whether in all samples the components are present in the same weight proportion. Milk is shown to be a mixture, for samples of milk differ widely in content of butter fat. One would classify baking powder as a mixture because different

types of baking powder have somewhat different properties and composition. On the other hand, baking soda is a pure chemical compound whether purchased as baking soda at the grocer's, as bicarbonate of soda at the drug store, or as sodium acid carbonate in a chemistry laboratory.

Law of Definite Composition. — The examples just given indicate that compounds contain a definite proportion by weight of constituent elements; for example, a certain weight of iron combines with a certain weight of sulphur to form iron sulphide. If the unheated mixture contains more sulphur than the iron needs to make iron sulphide, there will be unchanged sulphur in the heated product; or if the mixture contains iron in excess of that needed by the sulphur, there will be unchanged iron in the product. The iron sulphide formed in any case contains a definite proportion by weight of iron and sulphur. Likewise, all samples of sugar contain carbon, hydrogen, and oxygen in a definite proportion by weight, and all samples of magnesium oxide contain magnesium and oxygen in a definite proportion by weight. These are a few illustrations of the **law of definite composition** which states that every pure compound is composed of a definite proportion by weight of constituent elements.

Molecules. — Chemists have shown that an element or compound may be powdered or ground up by mechanical means to a very fine state of division and still retain the properties of the original matter. Further disintegration by chemical means will give substances having different properties. The molecule is the smallest unit into which a substance may be divided and still retain all the properties of the mass of matter. Thus the chemist conceives that sugar may be separated into molecules too infinitesimal to be visible even with the highest powered microscope and yet retain all the properties of sugar.

Some idea of the small size of an individual molecule and the number of them occurring in a given volume may be obtained if we consider how widely they may be scattered, or how large a volume may be affected by a small weight of substance. If one

gram of sugar is dissolved in water, the molecules become scattered throughout the solution in such a way that every portion of a gallon or more of liquid would taste sweet. *How small must the molecules be*, in order that one gram of sugar could contain enough of them to be distributed throughout a gallon of water. Because molecules are so small and can be dispersed so widely, a few drops of ginger extract contain enough molecules to flavor a large cake, and a few grams of dye to color large quantities of water or many yards of cloth.

Atoms. — Our experiments have indicated that the compound, sugar, may be decomposed by heat into simpler substances, as shown by the statement:



It may be shown, also, that water by electrolysis is resolved into the gaseous elements hydrogen and oxygen. The statement for the chemical change is:



It is evident that molecules of sugar and of water must be made up of smaller units of matter which, under the influence of energy, rearrange themselves to form other kinds of molecules. These small units, which we conceive to be taking part in chemical reactions, are called **atoms**. It is thus considered that molecules of water are made up of atoms of hydrogen and atoms of oxygen; that molecules of sugar consist of atoms of carbon, hydrogen, and oxygen. There are, in fact, ninety-two different kinds of atoms, one for each kind of element. A symbol, then, which we have used as an abbreviation for the name of an element, also represents an atom of an element.

The Chemist's Method of Expressing Atoms and Molecules. — The chemist uses a group of symbols, called a **formula**, to represent molecules of an element or compound. It is necessary that the formula should indicate the number of atoms of each kind in

the molecule. The formulas for most solid elements are the same as their symbols, and are represented as follows:

Zn.....one molecule of zinc
 Cu.....one molecule of copper
 Fe.....one molecule of iron
 5Mg.....five molecules of magnesium
 4C.....four molecules of carbon.

Experiments have shown that most gaseous elements have two atoms per molecule, as shown by the formulas:

O₂.....one molecule of oxygen
 H₂.....one molecule of hydrogen
 3Cl₂.....three molecules of chlorine
 2N₂.....two molecules of nitrogen.

Molecules of compounds contain at least two, and often many different kinds of atoms. Formulas for compounds are determined by laboratory analysis. The results of the analysis show the number of atoms of each element in the molecule of the compound, as indicated by the subscripts in the following formulas:

H₂O.....one molecule of water
 5H₂O.....five molecules of water
 C₁₂H₂₂O₁₁.....one molecule of sugar
 3MgO.....three molecules of magnesium oxide
 FeS.....one molecule of iron sulphide.

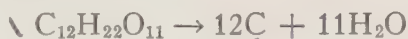
Equations. — In the foregoing pages attention has been called to several word statements which show the framework of chemical changes. They do not represent the energy change involved, nor do they indicate any conditions for bringing about the chemical change. They do show that in a chemical change, molecules are taken apart and the constituent atoms rearrange themselves to form new molecules with different properties. A familiar illustration is the heating of sugar, for which the chemical change is represented by the word statement:



Having learned the formulas for these substances, we can use them in expressing this chemical change as follows:



This chemical equation is not entirely satisfactory as it is written, since it does not show the number of molecules of carbon and of water that are formed from each sugar molecule. Since there are twelve atoms of carbon in each sugar molecule, and each carbon molecule consists of one atom, twelve carbon molecules must be formed. In the same way, twenty-two atoms of hydrogen and eleven atoms of oxygen can arrange themselves to form eleven molecules of water (H_2O). The equation may be written as follows to show this condition:



This will be read: One molecule of sugar gives twelve molecules of carbon and eleven molecules of water. Such a statement is known as a **balanced equation**, which means that the numbers of molecules on the two sides of the equation are adjusted in such a way that the same number of atoms of each element enter into the reaction as are found in the products. Since chemical changes are simply rearrangements of atoms, equations are always balanced to show what has happened to each atom that enters into the reaction.

Equations may be written for any chemical reaction if the formulas of the reactants and products are known. For example,



Representing these with formulas, we have:



Balancing the equation, we find that to get two atoms of oxygen, two molecules of water will be required, and these in turn will form four atoms or two molecules of hydrogen. The balanced equation is:



Summarizing the method of writing an equation — the formulas for the substances entering into an equation will be written on the left side of an arrow, and the formulas for the products are

written on the right side of the arrow. Finally, the equation is balanced by the process described above.

QUESTIONS AND PROBLEMS

1. In terms of atoms, tell how molecules of compounds differ from molecules of elements.
2. In terms of molecules, compare the composition of mixtures with the composition of pure substances (compounds or elements).
3. Describe the three characteristics that may be used to distinguish between a mixture and a compound. Use an example of each substance and tell why the illustration satisfies the requirements of a mixture and of a compound.
4. Classify the following as elements, compounds, or mixtures: gold, air, water, baking soda, baking powder, sugar, charcoal, salt, sulphur, candy, iron, iron rust, syrup.
5. Choose from the table of elements in the appendix those which are familiar. Classify these as metals or non-metals. From this table choose a metal that has a yellow color, a metal that will burn, a non-metal with a yellow color, an element that is a colorless gas, a metal used in making cooking utensils, two non-metals that will burn, a black non-metal.
6. Name two white compounds, a compound that melts easily, a compound that will not burn.
7. Distinguish between symbol and formula, using illustrations of each.
8. Use formulas to represent:
 - (1) two molecules of oxygen
 - (2) five molecules of zinc
 - (3) one molecule of water
 - (4) six molecules of sugar
 - (5) three molecules of chlorine gas
 - (6) two molecules of carbon.
9. Write in words, the meaning of the following expressions:

(1) $2\text{H}_2\text{O}$	(5) 8Zn
(2) 3Cl_2	(6) 3O_2
(3) 5FeS	(7) 3N_2
(4) 2MgO	(8) $2\text{C}_{12}\text{H}_{22}\text{O}_{11}$
10. Using the following correct formulas for compounds, give the number of atoms of each element in the molecule:
 - (1) CaCO_3 calcium carbonate (marble)
 - (2) NaOH sodium hydroxide (lye)
 - (3) Fe_3O_4 iron oxide (iron rust)
 - (4) NH_3 ammonia
 - (5) $\text{Mg}(\text{OH})_2$. . . magnesium hydroxide (milk of magnesia)

- (6) Na_2CO_3 . . . sodium carbonate (washing soda)
- (7) $\text{C}_{10}\text{H}_{16}$. . . moth-balls
- (8) $\text{C}_2\text{H}_5\text{OH}$. . . alcohol
- (9) $\text{KAl}(\text{SO}_4)_2$. . alum
- (10) $\text{Ca}_3(\text{PO}_4)_2$. . calcium phosphate
11. Write a word statement to correspond to each of the following chemical reactions; use formulas to put the word statement into a balanced equation:
 - (1) burning magnesium in oxygen to form magnesium oxide
 - (2) iron with oxygen forms iron rust (Fe_3O_4)
 - (3) heating sugar to form carbon and water
 - (4) burning hydrogen in oxygen to form water
 - (5) lye (NaOH) may be decomposed by electricity to form sodium, oxygen, and hydrogen
 - (6) nitrogen gas combines with hydrogen gas to form ammonia (NH_3)
 - (7) the reaction of steam with iron forms iron oxide and hydrogen.
12. $2\text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$
 - (1) Name and state the number of molecules of each substance entering into reaction; in the products. (See question 10 for names of compounds.)
 - (2) How many atoms of each element enter into the reaction? How many atoms of each element in the products?
 - (3) Is the equation balanced? Give reason for your answer.
13. Balance the following equations:
 - (1) $\text{N}_2 + \text{H}_2 \rightarrow \text{NH}_3$
 - (2) $\text{Zn} + \text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2$
 - (3) $\text{Mg} + \text{O}_2 \rightarrow \text{MgO}$
 - (4) $\text{Fe} + \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3$
 - (5) $\text{Al}_2\text{O}_3 + \text{HCl} \rightarrow \text{AlCl}_3 + \text{H}_2\text{O}$
 - (6) $\text{Na} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{H}_2$
 - (7) $\text{Ca}(\text{OH})_2 + \text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O}$
 - (8) $\text{Al} + \text{HCl} \rightarrow \text{AlCl}_3 + \text{H}_2$

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CHAPTER III

THE CHEMISTRY OF WATER

Importance of Water. — Water is so abundant on the earth, so universal in its use, so ever-present in all nature around us, that we scarcely think of it as a chemical substance. Nevertheless we shall continually have occasion to use it in our experimental work. A large number of the compounds that we study in the laboratory are used in water solution, because many of the chemical reactions take place more quickly and easily in the presence of water. We have probably noticed that baking powder, a mixture of two compounds, reacts immediately when water is added. We shall find in the laboratory that many substances that appear to be dry, such as borax and washing soda, contain water in combination and evolve it when heated. We shall learn that certain active metals react with water or steam. Water is a relatively simple compound and a study of its composition has helped scientists to learn about the microscopic and submicroscopic structure of matter. Because it is familiar to all, and because it has a simpler composition than most compounds, it serves as an excellent basis for our study of the chemistry of matter.

Physical Properties of Water. — Water is known to every one as a colorless, odorless liquid, which freezes to a solid when cooled and changes to a vapor when heated. These changes in properties are physical changes only (Chapter I), because there is no change in composition or in chemical properties.

An important physical property of water is its ability to absorb heat. More heat energy (calories) is required to raise the temperature of a given weight of water than to raise the temperature of an equal weight of any other substance. In the same way, more heat is given off when hot water cools to room temperature than when an equal weight of any other substance at the same temperature is

cooled. In other words, the specific heat, which is the number of calories required to raise the temperature of one gram of a substance through one degree centigrade, is higher for water than for any other kind of matter. The absorption or liberation of heat by water has many applications so familiar to us that we scarcely stop to think that there is an important principle therein involved. A few examples follow: in making candy, the hot sugar syrup is cooled by surrounding the pan containing it with cold water; we use a hot-water bottle as a source of heat because the water radiates more heat energy than other heated substances; water is used in automobile radiators to absorb the heat developed by the burning of gasoline in the engine. The fact that large bodies of water tend to regulate the temperature of the surrounding country is another illustration of the absorption and liberation of heat by water. The air is cooled in summer through the absorption of heat in raising the temperature of the water, and in winter heat is radiated from the water, making the surrounding air warmer.

We expect a substance to expand when heated and to contract when cooled. When water is cooled it contracts until it reaches 3.8°C. , then it expands as it is cooled further to 0°C. , and at this temperature it changes to ice. Thus one cubic centimeter of water at 3.8°C. represents a greater weight of water than the same volume at any other temperature. For this reason, in the metric system, the unit of weight, the gram, is defined as the weight of one cubic centimeter of water at 3.8°C. , the point of greatest density. At other temperatures one cubic centimeter of water weighs slightly less than one gram.

Solutions. — Water has the property of mixing with certain substances so completely that, as far as one can tell by a study of the physical properties, the mixture is homogeneous. These mixtures are called solutions. Thus when sugar or salt dissolves in water, a single drop of the resulting solution has the same properties as every other drop. That there is no chemical change in the sugar, salt, or water is evident because the solution has the properties of the substance dissolved. In other words, a solution of a colored substance is colored, and a solution of a sweet or sour

substance is sweet or sour. Moreover, if the water is removed by evaporation, the substance left is identical with the original. The substance that changes its physical state and is dispersed in a solution is called the **solute**. The solute may be a solid such as salt or sugar, a liquid such as alcohol, or a gas such as chlorine or air. The substance in which the solute is dispersed is called the **solvent**. Water is a common solvent and is used for most of the solutions with which we are familiar. However, other solvents are known. Iodine is usually used as a solution of the solid iodine in alcohol; many types of finger-nail polish are solutions of collodion in banana oil. When the solvent (banana oil) evaporates, the film of collodion holds the color on the nail. To remove the polish, we dissolve it in the same or a similar solvent. Kerosene or gasoline are used often as solvents to remove spots from clothing because they dissolve fat or grease better than water. In fact, the solvent may even be a gas or a solid. We speak of water vapor dissolved in air, which is a gas. Glass and artificial gems may be solid solvents colored by small quantities of minerals dissolved in them. A **solution**, then, may be defined as matter in any one of three physical states, solid, liquid, or gas, dispersed homogeneously throughout any dispersion medium. Solutions in water, since they are the most familiar to us, will be used as examples in this chapter.

Solubility. — It should be noted that solutions differ from heterogeneous mixtures, like those of sand and water or salt and pepper, in that the amount of the solute that can be dispersed or dissolved in a given volume of solvent is usually limited; for example, after a certain definite amount of sugar has dissolved in water, any excess sugar added to the solution will not dissolve but will settle to the bottom of the container (assuming there is no change in temperature). The amount of substance that can be dissolved in a given amount of water depends principally on the nature of the substance and the temperature of the solution. The weights of some familiar substances that will dissolve in 100 g. of water at the temperatures indicated are given in Table IV.

TABLE IV

SOLUBILITY

Weights of solutes dissolved in 100 grams of water

<i>Solute</i>	<i>Grams at 20° C.</i>	<i>Grams at 100° C.</i>
Sugar	203.900	487.200
Salt	36.200	39.800
Chalk	0.001	0.001
Oxygen	0.004	0.000
Ether	8.300	0.000

Saturated, Unsaturated, and Supersaturated Solutions.—When a solution contains all the solute that will dissolve at a certain temperature, it is said to be a **saturated** solution. Any additional solute when placed in contact with such a solution is not dissolved. According to data in Table IV, a solution that contains 203.9 g. of sugar in 100 g. of water at 20° C. is saturated. A solution that contains less solute than will dissolve at the given temperature is **unsaturated**. It follows that a sugar solution at 20° C. containing less than 203.9 g. of sugar in 100 g. of water is unsaturated.

Supersaturated solutions, which contain more solute than can be dissolved under existing conditions, may be prepared from sugar or from several other compounds. Sugar syrup is one of the most familiar examples of a supersaturated solution. A syrup, saturated with sugar at 100° C., contains 487.2 g. of sugar in 100 g. of water (Table IV). If this syrup is allowed to cool to 20° C., keeping all the sugar in solution, it is a supersaturated solution because the syrup contains more sugar than would dissolve in 100 g. of water at 20° C. by stirring sugar and water together. The syrup made at 100° C. and cooled to 20° C. actually contains an excess of sugar equal to the difference between 487.2 g. and 203.9 g., or 283.3 g. The preparation of most **supersaturated** solutions will depend on making a saturated solution at some given temperature and then cooling the saturated solution to any lower temperature, keeping all the solute in solution.

A supersaturated solution is in an unstable condition; for ex-

ample, stirring or jarring the mixture may cause the excess solute to crystallize; or contact with a crystal of solid solute may bring about crystallization of the excess material. The amount of sugar crystals which crystallize from a sugar syrup saturated at 100°C . and cooled to 20°C . will be 283.3 g., as before mentioned. Honey, jelly, and thick syrups are supersaturated solutions, and they often form sugar crystals when disturbed, or on addition of some solid matter.

It is fortunate for the candy-maker that sugar forms supersaturated solutions, as they are the basis of all soft candies. Alum and saltpeter, on the other hand, dissolve rapidly in hot water, but on cooling, the excess of solute forms crystals. Therefore, as the solution cools, one never has a supersaturated solution but only a saturated solution at any given temperature, in contact with solid crystals.

Since all solutions are homogeneous and clear, one cannot determine their saturation by appearance only. It is possible, however, to distinguish between the solutions by addition of a crystal of solute, as suggested above. When solid solute is added to water or to an unsaturated solution, the tendency of the substance to disperse through the liquid causes the particles of the crystal to push out and away from the solid. In other words, solid particles dissolve as long as the solution is unsaturated. When solid solute is added to a saturated solution, we say the crystal does not dissolve. However, careful observation shows that, in time, the crystal may change in shape though not in weight. To account for this, we consider that some pieces of crystals have a tendency to dissolve while others have a tendency to crystallize; hence one action exactly counterbalances the other and is known as a condition of **equilibrium**. In a supersaturated solution, the addition of solid solute causes the formation of larger crystals and more undissolved solute, because the tendency for particles of solute to form on the crystals is much greater than the tendency for the solute to dissolve.

A knowledge of the properties of solutions is important in making fudge or fondant. A hot saturated sugar solution is allowed to cool to make a highly supersaturated solution. If

sugar crystals are formed quickly from this supersaturated solution by stirring and beating, the crystals are minutely small, and a soft, creamy candy results. (See Colloids, Chapter XXXI.)

Concentrated and Dilute Solutions. — We may distinguish more easily between a dilute and a concentrated solution if we use familiar substances for illustrations. Maple syrup is an example of a concentrated solution, and maple sap, as it comes from the tree, is an example of a dilute solution. In the former there is a large proportion of solute (sugar) to solvent, while in the latter there is very little solute in the large volume of sap. In the laboratory we use dilute and concentrated solutions of many reagents, and the terms have the same meaning as in the illustration just given. The words dilute and concentrated do not state just how much solute is present in a solution but only which solution has the greater proportion of solute.

Percentage Solution. — The percentage of solute in a solution is usually expressed as grams of solute in each 100 g. of solution. Occasionally it means grams of solute in each 100 c.c. of solution. It is often necessary in experimental and industrial laboratories to express concentrations in exact percentage; for example, large food concerns using vinegar are not satisfied to know that it is "strong" or "weak," "concentrated" or "dilute." The concentration of acetic acid in vinegar is usually expressed in percentage, which means, in this case, the grams of solute in 100 c.c. of solution. Thus a vinegar that contains four grams of acetic acid in each 100 c.c. is a 4 per cent solution.

Chemical Properties of Water. — Water is a very stable compound. It has been shown that heating water to 100° C. does no more than change its physical state from a liquid to a vapor, and attempts to decompose it by heat alone have not met with success. Only when steam is heated to temperatures as high as 2,000° C. and above, is there any tendency for it to decompose into the elements of which it is composed. These gases have been proved to be hydrogen and oxygen. The decomposition of water

is accomplished more readily by the use of electricity as described in the next paragraph. It will be shown that the gases obtained are oxygen and hydrogen, and that the process may be used to determine the volume ratio of hydrogen to oxygen in water.

Composition of Water by Volume. — Method I. Analysis.

When a compound is decomposed to determine the proportion in which the constituent elements are present, the process is known as analysis. The analysis of water is accomplished by an apparatus devised to collect, in separate chambers in which the volume of gas may be read directly, the oxygen and hydrogen formed. An apparatus that may be used is shown in Figure 4. In this experiment, called electrolysis, the apparatus is filled with acidulated water until there is no air in the outer tubes. Wires, connected with a source of electricity, are attached at A and A' and terminate in the platinum electrodes which are within the graduated tubes of the apparatus. As the current (direct) passes through the water, oxygen gas collects at the positive electrode, and hydrogen gas collects at the negative electrode. The gases rise through the liquid to the top of the tubes and displace the water, which flows back into the reservoir B. The gases collect in the inverted tubes, and their volumes can be read directly from the graduations. The apparatus is shown in Figure 4, which is a detailed diagram of the electrolysis setup. It features a central U-shaped tube with two vertical graduated tubes on either side. The central tube has a bulb at the top labeled 'B'. The two side tubes have stopcocks labeled 'C' and 'C'' at the top. At the bottom of the central tube, there are two electrodes labeled 'A' and 'A'' with '+' and '-' signs respectively. The entire apparatus is mounted on a tripod stand.

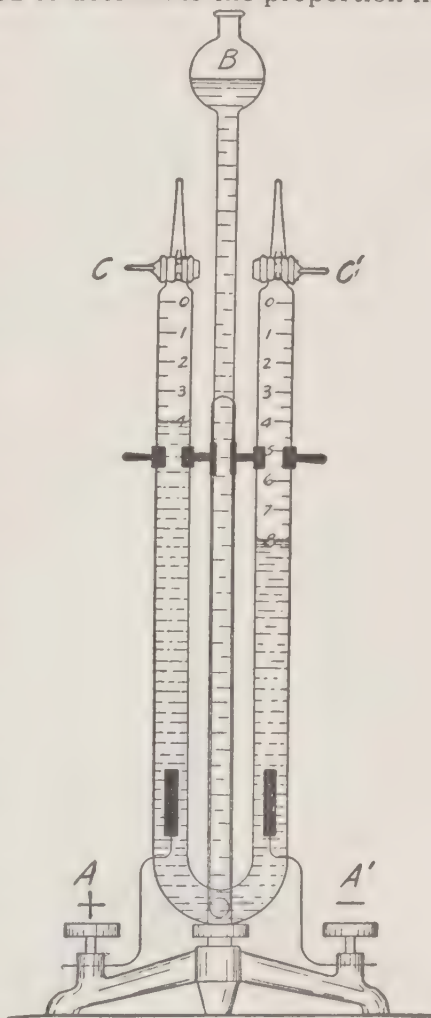


FIG. 4. Electrolysis of Water

After reading the volume of each gas obtained, a simple test may be used to prove the presence of the oxygen and the hydrogen. The gas obtained by opening the stop-cock C will cause a glowing splint to glow more brilliantly, proving the presence of oxygen, while the gas obtained by opening the stop-cock C' will burn with a bluish flame, showing that it is hydrogen.

During the decomposition of water, it may be noted that the tube containing hydrogen fills twice as rapidly as the tube containing oxygen. Thus it is evident that hydrogen and oxygen gases are formed in the ratio of two volumes of hydrogen to one volume of oxygen; that is, ten cubic centimeters of hydrogen for every five cubic centimeters of oxygen, or any similar volume ratio. If the volume of water disappearing could be measured as steam at the same temperature and pressure as the hydrogen and oxygen, the following volume ratio would be obtained:

two volumes of steam \rightarrow two volumes of hydrogen gas
+ one volume of oxygen gas

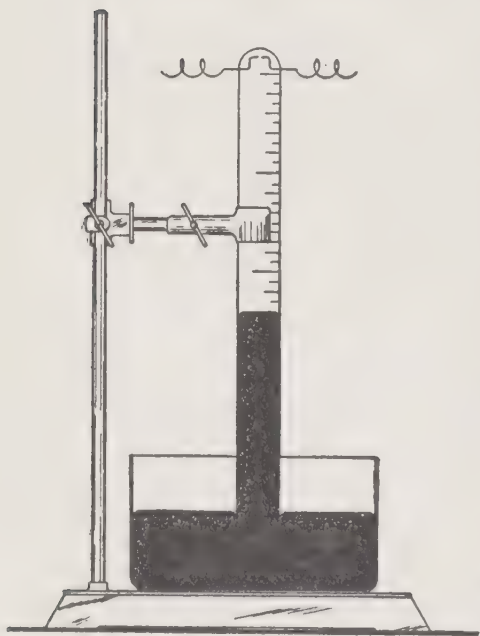


FIG. 5. Eudiometer Tube for Synthesis of Water

(It should be understood that the word *volume* or *volumes* may be replaced by some unit of measure, such as *cubic centimeter*, *liter*, or *quart*.) This same ratio of hydrogen to oxygen is obtained by synthesis of water as described in the next paragraph.

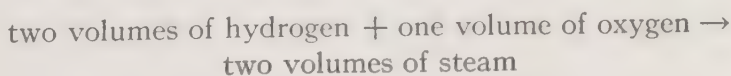
Method II. Synthesis. When elements are combined to form a compound in order to determine the quantitative ratio in which they occur, the process is called synthesis. Water may be synthesized in a eudiometer tube, which is illustrated in Figure 5. The tube is de-

signed for the measurement of gases and is graduated in cubic centimeters. Two platinum wires, with a small gap between the ends, are fused into the glass near the top of the tube. Electric connection is made by means of these wires, and a spark may be made to pass between the two points within the eudiometer tube. If the tube is filled with mercury and inverted over mercury held in a container, the mercury may be displaced by a mixture of hydrogen and oxygen, the volumes of which may be determined. There is no reaction between the gases of this mixture until an electric spark is passed through to ignite them. Chemical union then takes place until one of the gases is exhausted. The volume of the gas that is left is measured, and from this the ratio in which the two gases combine is easily calculated.

Typical results from such an experiment are as follows:

	<i>c.c. of gas</i>
(a) Volume of hydrogen passed into tube	20
(b) Volume of mixed gases, after oxygen is added	35
(c) Volume of oxygen added (b - a)	15
(d) Volume of gas (oxygen) after ignition	5
(e) Volume of oxygen combined (c - d)	10

The results indicate that 20 c.c. of hydrogen combine with 10 c.c. of oxygen. Repeated syntheses always show the volume ratio to be two volumes of hydrogen combined with one volume of oxygen. The volume of water, as liquid, formed by the combination is too small to be measured. However, if the temperature of the eudiometer tube is kept above 100° C. by enclosing it in a steam jacket, the gases, hydrogen and oxygen, combine to form steam. Thus the volume of all may be measured as gases. If exactly 20 c.c. of hydrogen and 10 c.c. of oxygen were introduced into the eudiometer tube at 100° C. and ignited by the electric spark, the volume of steam formed would be 20 c.c., the same as the original volume of hydrogen. In other words:



Thus by synthesis as well as by analysis, water is shown to be a

compound made up of the elements hydrogen and oxygen, and the volume relationship of each is indicated.

Composition of Water by Weight. — Experiments show that when oxygen and hydrogen combine, the weight of the water formed is exactly equal to the weight of the mixed gases. This is in accord with the law of conservation of matter as stated in Chapter I. Since the weights of liters of gases at definite temperatures and pressures may be determined, it is possible to calculate the weights of hydrogen and of oxygen entering into reaction and the weight of water formed. For example, one liter of oxygen weighs 1.429 g. This amount of oxygen combines with two liters of hydrogen, which weigh 2×0.0898 g. or 0.1796 g. The weight of steam or water formed is the sum of the weights of hydrogen and oxygen entering into reaction, or $1.429 + 0.1796 = 1.6086$ g. In terms of a single statement:

0.1796 g. of hydrogen + 1.429 g. of oxygen \rightarrow 1.6086 g. of water

This is in the ratio of one part by weight of hydrogen to 7.95 parts by weight of oxygen, making 8.95 parts by weight of water or steam. Every sample of water contains this same proportion by weight of hydrogen and of oxygen — another illustration of the law of definite composition.

QUESTIONS AND PROBLEMS

1. What properties of water did you know before studying this chapter? What new properties of water have you learned from this chapter?
2. How is a solution different from and how is it similar to other mixtures?
3. Distinguish between *solute* and *solvent*. Name three common solvents, other than water, which are used in the home.
4. How could one distinguish between a saturated, an unsaturated, and a supersaturated solution?
5. Why may lemonade sweetened with a syrup be made sweeter than when sweetened by adding sugar?
6. Classify the following solutions at 20° C. as (a) dilute or concentrated, (b) saturated, unsaturated, or supersaturated.
 - (a) 8 g. of salt in 1,000 g. of water
 - (b) 30 g. of salt in 100 g. of water
 - (c) 40 g. of sugar in 500 g. of water
 - (d) 60 g. sugar in 25 g. water
 - (e) 3.62 g. salt in 10 g. water
 - (f) 8.3 g. ether in 200 g. water
7. Diagram and describe the apparatus used for the electrolysis of water. Explain how it is used to determine the composition of water.

8. Distinguish between the terms *analysis* and *synthesis*.
9. Diagram and explain the method of determining the composition of water by synthesis.
10. What is the volume ratio of hydrogen to oxygen in water? the weight ratio?
11. What volume of steam is produced when 1,000 c.c. of hydrogen combine with 500 c.c. of oxygen?
12. What weight of oxygen would be combined with 3.26 g. of hydrogen to produce 29.17 g. of water?
13. What volumes of hydrogen and oxygen would be used in forming 50 c.c. of steam in a eudiometer? What is this process called?
14. What weight of water would be necessary to form 8 kg. of hydrogen and 63.5 kg. of oxygen by decomposition? What is this process called?
15. How many grams of water would be decomposed by electrolysis to form 6 g. of hydrogen and 47.64 g. of oxygen?
16. If 50 c.c. of hydrogen and 40 c.c. of oxygen were mixed in a eudiometer and ignited, which gas would be left over? What volume of the gas would be left? If the gases were kept above 100° C., what volume of steam would be formed?
17. What volume of hydrogen will combine with 45 c.c. of oxygen? What volume of steam will be formed?
18. What weight of oxygen will combine with 4 g. of hydrogen? What weight of steam or water will be formed?
19. If 30 c.c. of hydrogen and 10 c.c. of oxygen are mixed in a eudiometer and ignited, what volume of steam will be formed? Which gas and how many c.c. of it will be left uncombined?
20. What is the volume occupied by 24 g. of hydrogen, and by 24 g. of oxygen? (1 liter of hydrogen weighs 0.0898 g., and 1 liter of oxygen weighs 1.429 g.) When 24 g. of hydrogen are mixed with 24 g. of oxygen and ignited to form water, which gas will be left over, uncombined? How many grams of the gas will be uncombined? How many grams of water will form?

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CHAPTER IV

OXYGEN

Occurrence of Oxygen. — It has been stated that oxygen is the most abundant of all the ninety-two elements. In the free elementary state, oxygen comprises one fifth by volume of the air nearest the earth. Oxygen is found in some compounds which occur in the natural state, such as water, H_2O ; starch, $\text{C}_6\text{H}_{10}\text{O}_5$; limestone, CaCO_3 ; sand, SiO_2 ; iron ore, Fe_3O_4 ; and the ores from which many metals other than iron are made. In the form of compounds oxygen comprises more than one half of the weight of the soil, sand, and rocks forming the earth's crust, a large percentage of the weight of all living matter, and seven eighths of the weight of water.

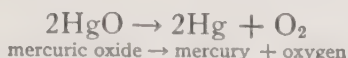
Preparation of Oxygen. — 1. *Electrolysis of Water.* This method, described in Chapter III, showed that acidified water could be decomposed into the elements oxygen and hydrogen as indicated by the equation:



2. *Decomposition of Certain Compounds Containing Oxygen.* Oxides are compounds containing oxygen and one other element. Some examples of oxides are mercuric oxide, HgO ; magnesium oxide, MgO ; manganese dioxide, MnO_2 ; copper oxide, CuO ; and carbon dioxide, CO_2 . Mercuric oxide, HgO , is the only compound in the list that is sufficiently unstable to be decomposed readily by heat. Manganese dioxide, MnO_2 , may decompose to give up part of its oxygen if heated to a high temperature.

It is of historical interest that mercuric oxide is one of the first compounds from which oxygen was obtained. When red mercuric oxide is heated in a test tube, there is visible evidence of chemical change. Tiny globules of liquid mercury collect on the cool parts

of the tube, and the presence of oxygen gas may be determined by the bright burning of a glowing splint thrust in the tube where the reaction occurs. The reaction may be represented by the following equation:



A more complex substance that readily gives up oxygen when heated is the white, crystalline compound potassium chlorate, KClO_3 . The following equation indicates the chemical reaction:

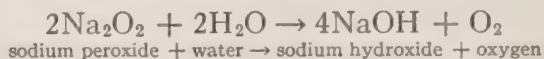


As shown by the formula, potassium chlorate contains the elements potassium, chlorine, and oxygen. Potassium chloride is a binary compound composed of two elements, potassium and chlorine. On heating pure potassium chlorate oxygen is evolved only when the compound is heated much beyond its melting-point. If a mixture of potassium chlorate and a few grains of manganese dioxide is heated, oxygen is liberated freely at a temperature below the melting-point of potassium chlorate. Although the manganese dioxide does not give up any of its oxygen and remains chemically unchanged after the process, it causes potassium chlorate to give up its oxygen more readily. This is an interesting phenomenon — one of the many examples of the use of chemical substances which change rate of reaction. A **catalytic agent** is a substance which is known to influence the rate of a chemical reaction but does not change in composition during the reaction. Thus manganese dioxide acts as a catalytic agent in the decomposition of potassium chlorate. The process of accelerating or retarding the reaction is called **catalysis**.

3. *Separation of Oxygen from Nitrogen in the Air.* The air we breathe consists in large part of a mixture of the gaseous elements oxygen and nitrogen. It contains also small percentages of carbon dioxide, water vapor, and other gases. Air may be purified by removal of water vapor and carbon dioxide, and then by sufficient cooling and compression the gases may be condensed to a mixture of liquid oxygen and liquid nitrogen. The two liquids of the mix-

ture do not have the same boiling-point, and if the temperature is allowed to rise, the nitrogen will boil away at its boiling-point, -195.5°C. , leaving the liquid oxygen. The oxygen may be allowed to boil at its boiling-point, -182.5°C. , and may be collected in a separate vessel. There is no chemical change involved in the liquefaction of air or in the separation of the elements nitrogen and oxygen by fractional boiling. Moreover, the separation is somewhat incomplete, and oxygen prepared by this method contains some nitrogen mixed with it.

4. *Reaction of Sodium Peroxide with Water.* Sodium peroxide, Na_2O_2 , is a white, unstable solid which reacts with water to give up part of its oxygen. The equation for the chemical change is:



Choice of Method. — In the laboratory, each student prepares oxygen so that he may observe some of the properties of the gas. The apparatus used should be comparatively simple and easily assembled; since only small quantities of oxygen are made, the cost of the materials used is a secondary factor. The heating of compounds which readily give up oxygen and the addition of water to sodium peroxide are methods easily adapted for the laboratory preparation of oxygen.

When industrial concerns make oxygen for use in laboratories or hospitals or for oxyacetylene blowpipes, they are more interested in a cheap source of the element, since large quantities of the initial material are needed. On the other hand, the apparatus is in use constantly, and an expensive and complex apparatus is practicable if it allows the use of inexpensive materials. Since air and water each contain a large percentage of oxygen, the evaporation of liquid air and the electrolysis of water are considered suitable as methods for the commercial preparation of oxygen.

Properties of Oxygen. — *Physical.* Since oxygen is around us in the air, we know it to be an odorless, colorless, and tasteless gas. It is slightly soluble in water, and when in solution it improves the taste of the water and has a tendency to kill micro-organisms.



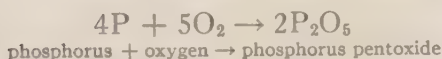
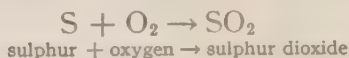
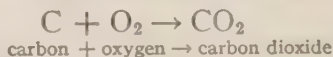
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OXYGEN MASK

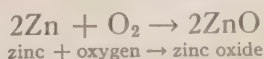
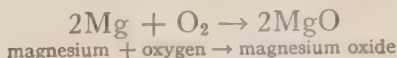
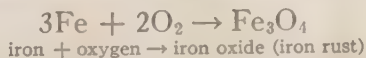
Oxygen, on which the high altitude flier's life depends, can be supplied by this mask which Dr. Alvan L. Barach and Dr. Morris Eckman, of Columbia University College of Physicians and Surgeons, devised for airplane pilots and for heart disease or pneumonia patients. Advantages of the mask reported by Dr. Barach to the Aero Medical Association are: (1) easier breathing, because the carbon dioxide content is one-tenth that in masks with rebreathing bags, and (2) provision for constant oxygen percentage in the inspired air.

It gives water the sparkling appearance that is often seen near rapids and waterfalls. Oxygen is less soluble in hot water than in cold water. As a result, when cool water stands in a warm place, bubbles of dissolved oxygen will be evolved and will collect on the sides of the container. When cold water is heated, these bubbles may be seen some time before the water is near the boiling-point. The absence of dissolved oxygen in water leaves it with a flat, insipid taste. Oxygen is slightly heavier than air. At the same temperature and pressure, one liter of oxygen weighs 1.429 g., while one liter of air weighs 1.292 g. Oxygen may be cooled and compressed to a liquid of pale-blue color or to a pale-blue solid. The solid will melt at -219°C . and the liquid boils, as has already been noted, at -182.5°C .

Chemical. Oxygen is active at high temperatures, combining with almost all other elements. We have noted that hydrogen will burn in oxygen to form water. The reactions of non-metals with oxygen are illustrated by the following equations:

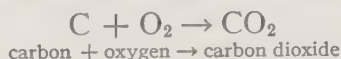


Most metals unite directly with oxygen. The more active metals, such as sodium, unite spontaneously; magnesium, if heated slightly, combines readily with oxygen, giving a brilliant white light; other metals which are not so reactive combine slowly with oxygen. Typical equations for the reactions are the following:



The reaction used as a **test for oxygen** gas has been mentioned (Chapter III). When a glowing splint is placed in the presence of

oxygen gas, the glow becomes very brilliant and a flame appears. The reaction is the burning of the wood, which is mostly carbon. Consequently, the equation is represented by



Burning, Combustion, Oxidation. — When any substance combines with oxygen, as suggested in the foregoing equations, the reaction is called **oxidation**. If heat and light are evolved, as when magnesium is ignited and combines with oxygen, the reaction is called **burning**. When wood, coal, or any substance burns, combination with oxygen occurs, and equations similar to the ones given may be written. The term **combustion** is used when one refers to any chemical reaction in which heat and light are evolved. The direct combination of magnesium with oxygen, of iron with sulphur, or of iron with chlorine are processes of combustion when heat and light are given out during the reaction.

When a gas has the property of combining with a substance and of giving off heat and light in the process, it is said to support combustion. Air has the property of supporting combustion because substances combine with the oxygen in it. If a substance that is burning slowly or glowing in the air is thrust into pure oxygen, the glow becomes much more brilliant because there is more oxygen present to increase the rate of reaction. Imagine the delight and astonishment of the first chemists who obtained oxygen when they found that the gas they had prepared was so active. Joseph Priestley, discoverer of oxygen, called it “good air” because he found that a candle burned more brilliantly in it, and that a mouse lived in a bottle of the oxygen much longer than in the same quantity of ordinary air.

Kindling Temperature; Spontaneous Combustion. — A piece of the metal magnesium in contact with the oxygen of the air will slowly display a deposit of magnesium oxide on its surface. If the magnesium is heated in the presence of oxygen or air, rapid oxidation or combustion takes place with evolution of heat and light. At the **kindling temperature** of a substance, oxidation becomes sufficiently rapid to generate enough heat to produce a flame. It

is known that spontaneous combustion often occurs when oily cloths accumulate or when large amounts of coal, grain, hay, sawdust, or other combustible matter are stored in a large pile. Probably an air space is formed within the mass of material in which slow oxidation occurs, and heat is generated by the reaction. If the heat is carried away by air currents, spontaneous combustion never occurs. However, when the oxidation takes place within a large amount of stored material, the heat of reaction is not carried away but accumulates, and the increased temperature accelerates the reaction. When the material becomes heated to its kindling temperature, active burning or spontaneous combustion occurs.

Rate of Oxidation. — You have probably noted in the laboratory that the time required for chemical reactions to take place varies with each chemical reaction and with the circumstances. For example, a match burns easily and quickly, while copper wire has to be held in the flame several minutes before any change is evident. In the home we have seen pine sticks burn quickly and vigorously, while hard coal or charcoal glows quietly and burns slowly. A pine stump burns much more slowly than kindling-wood. Iron rusts easily in moist air, while gold tarnishes much more slowly.

The rate with which any substance oxidizes depends primarily on the tendency of the substance to combine with oxygen. With any given substance, however, the rate of oxidation is controlled by three factors. (1) The rate of oxidation increases with the temperature. We have learned that while the reaction between hydrogen and oxygen is almost imperceptible at low temperatures, it is explosive at higher temperatures. Countless experiences have taught us that fuels must be heated to their kindling temperature before combustion can start. (2) A catalytic agent may increase the rate of oxidation; for example, hydrogen and oxygen combine at low temperatures in the presence of platinum black. (3) The surface exposed and the concentration of the oxygen and the material to be oxidized affect the rate of oxidation, since chances of contact between the reacting substance depend on these factors. This is the reason that substances burn more vigorously in pure oxygen than in air. Finely divided wood burns more quickly than

large sticks because there is more surface in contact with the oxygen of the air. We shall find that these three factors are important in controlling the rate of all chemical reactions.

Formulas and Names of Compounds. — In the preceding paragraphs the names of many new compounds have been introduced. Chemical names usually suggest the elements of which the compound is composed; for example, magnesium oxide contains magnesium and oxygen, and potassium chloride contains potassium and chlorine. Most compounds with names ending in *-ide* contain only two elements. The compounds just cited are examples. Other illustrations are mercuric oxide, iron sulphide, and zinc chloride. The ending *-ate* is used for many compounds which contain oxygen in combination with two other elements. Thus, sodium sulphate contains the elements sodium, sulphur, and oxygen, while copper nitrate contains copper, nitrogen, and oxygen. A large group of compounds contain an oxygen-hydrogen radical in combination with a metal. These are known as hydroxides. Sodium hydroxide and calcium hydroxide are examples. Prefixes are sometimes used in naming compounds to designate the proportion in which the elements are combined. Thus, carbon dioxide contains two parts of oxygen with one part of carbon. The prefix *mono-* means "one," *di-* means "two," *tri-* means "three," *tetra-* means "four," and *penta-* means "five." The prefix *per-*, as in sodium peroxide, means that the compound contains an unusually large proportion of the element.

In so far as it is possible, the student should associate the formulas and names of compounds with materials used in the laboratory. The following are formulas needed in writing equations which have been studied:

H_2O	water	Fe_3O_4	iron oxide
KClO_3	potassium chlorate	MgO	magnesium oxide
FeS	iron sulphide	ZnO	zinc oxide
$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	sugar	HgO	mercuric oxide
CO_2	carbon dioxide	Na_2O_2	sodium peroxide
SO_2	sulphur dioxide	KCl	potassium chloride
MnO_2	manganese dioxide	NaOH	sodium hydroxide
	P_2O_5		phosphorus pentoxide

QUESTIONS AND PROBLEMS

1. What are the two principal components of the air? Describe the method by which oxygen gas is separated from the air.
2. Briefly describe the methods used commercially for making oxygen. What are the two sources of commercial oxygen? Give three uses of oxygen gas.
3. Name three compounds that may be used in the laboratory as sources of oxygen gas.
4. Diagram the apparatus used in the laboratory for the preparation of oxygen gas, and tell the purpose of each part of the apparatus. Tell what chemicals are used and the purpose of each substance.
5. Write equations for the reaction used in making oxygen gas, (a) from water, (b) from potassium chlorate, (c) from mercuric oxide, (d) by reaction of sodium peroxide with water.
6. Define the terms oxide, oxidation, catalytic agent, combustion, spontaneous combustion, combustible substance, kindling temperature. Name three substances with a low kindling temperature.
7. Write balanced equations for the following reactions:
 - (a) burning carbon in oxygen
 - (b) burning sulphur in oxygen
 - (c) burning phosphorus in oxygen
 - (d) burning magnesium in oxygen
 - (e) burning hydrogen in oxygen
 - (f) rusting of iron.
8. Give the formula and name for:
 - (a) a red oxide
 - (b) a black oxide
 - (c) a liquid oxide
 - (d) two gaseous oxides.
9. Name three factors that affect the speed of oxidation. Tell how two of these factors are involved in starting a campfire.
10. Give the physical properties of the following: sugar, potassium chlorate, manganese dioxide, mercuric oxide, magnesium oxide, oxygen, sulphur.

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CHAPTER V

ATOMIC WEIGHT. MOLECULAR WEIGHT

IN the preceding chapters we have used atoms in deriving formulas for compounds, and molecules in writing equations for chemical changes. In only a few cases has any mention been made of the weight of each element present in a compound or of the weight of matter entering into chemical reaction or in the products. We have mentioned (Chapter II) that in every pure compound there is a definite weight proportion of the constituent elements — the same for every sample of the compound. In this chapter, we shall describe the method used by the chemist in determining the weights of matter taking part in chemical reactions.

Avogadro's Hypothesis. — One of the fundamental theories of chemistry is the hypothesis formulated by an Italian physicist, Avogadro, who stated that "*equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules.*" Although it was first suggested as a theory and was considered improbable, it has now had sufficient proof to be known as an established truth. In fact, different scientists have determined the number of molecules in a volume of gas by six or more methods and all agree on the results. It is shown that at 0° C. and an atmospheric pressure of 760 mm., one liter of gas will contain 2.7×10^{22} , or 27,000,000,000,000,000,000 molecules. This is a stupendous number of molecules to be crowded into a liter vessel, but remember how small they are!

The weight of gas which fills a liter vessel at 0° C. and 760 mm. pressure may be determined by following laboratory directions. (See Section 2, Appendix.) For hydrogen (the lightest gas) this weight is 0.0898 g., for oxygen 1.429 g., for nitrogen 1.25 g., and for chlorine 3.16 g. Just as these values give a comparison of the weights of liters of gases (containing the same number of mole-

cules according to Avogadro's Hypothesis), they also give a comparison of the weights of molecules. That is, one molecule out of the liter of oxygen is $\frac{1.429}{.0898} = 15.88$ times heavier than hydrogen molecules. Likewise, nitrogen molecules are 14 times and chlorine molecules 35.5 times heavier than hydrogen molecules.

Atomic Weight and Molecular Weight. — These comparisons seem to give a good starting place for the determination of the weights of atoms and molecules. Chemists first chose as the unit with which to represent the weights of atoms and molecules the weight of the lightest atom, that of hydrogen. Later experiments showed that if the atomic weight unit were fixed at one sixteenth the weight of the oxygen atom, the atomic weights of many elements were whole numbers. The chemist has never given a name to this unit in the same way that we use grams or pounds.

On the basis of this value, "one sixteenth the weight of the oxygen atom," we may arrange the atoms of all elements in terms of how much heavier they are than this atomic weight unit. The atom of hydrogen weighs 1.008, the atom of chlorine weighs 35.457, the atom of aluminium weighs 26.97, and the heaviest atom, uranium, weighs 238.07. **Atomic weight** thus means the weight of the atom in terms of this atomic weight unit.

In terms of the same unit of weight, molecules of hydrogen (two atoms per molecule) weigh 2.016, molecules of chlorine (two atoms per molecule) weigh 70.914, molecules of aluminium (a solid element) weigh the same as the atom, 26.97. Molecules of water (H_2O) weigh 18.016, the sum of the weights of two atoms of hydrogen and one atom of oxygen. Likewise, molecules of sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) weigh 342.196. Thus, **molecular weight** tells the weight of the molecule in terms of the atomic weight unit.

Gram-Molecular Weight. — Because molecules are so infinitesimal, it is necessary to handle matter in terms of an aggregate of molecules instead of as single molecules, and to weigh matter in terms of the more convenient metric unit, the gram, instead of the atomic weight unit. Chemists have determined by many different

methods the relationship of the atomic-weight unit to the gram. They have been able to determine that it requires 6.06×10^{23} atomic-weight units to weigh one gram. On this basis, an aggregate of 6.06×10^{23} atoms or molecules will weigh the same in grams as one atom or molecule weighs in atomic weight units. For example — the value 2.016 as the molecular weight of hydrogen will be interpreted as 2.016 grams, the weight of 6.06×10^{23} molecules of hydrogen. Likewise 70.914 grams of chlorine, 26.97 grams of aluminium, and 18.016 grams of water is the weight of 6.06×10^{23} molecules of each substance. It is evident that we can use an aggregate of 6.06×10^{23} molecules, or a fractional or multiple part of this number of molecules, in studying chemical reactions while it is impossible to study reactions in terms of single molecules. The weight in grams of 6.06×10^{23} molecules of an element or compound is known as the **gram-molecular weight**. It is the molecular weight expressed in grams.

Gram-Atomic Weight. — While we do not handle matter as atoms, the term gram-atomic weight or gram-atom is significant. **Gram-atomic weight** is the weight in grams of 6.06×10^{23} atoms of an element. The weight is, for hydrogen, 1.008 g.; for chlorine, 35.457 g.; and for aluminium 26.97 g.

The Significance of a Formula. — We have learned that the chemist uses a formula to express molecules and to show the

TABLE V

<i>Substance</i>	<i>Formula</i>	<i>Gram-molecular weight</i>	<i>Number of molecules</i>
Hydrogen	H ₂	2.016	6.06×10^{23}
Oxygen	O ₂	32.000	6.06×10^{23}
Nitrogen	N ₂	28.016	6.06×10^{23}
Chlorine	Cl ₂	70.914	6.06×10^{23}
Carbon dioxide	CO ₂	44.000	6.06×10^{23}
Ammonia	NH ₃	17.032	6.06×10^{23}
Potassium chlorate	KClO ₃	122.557 *	6.06×10^{23}

* In all succeeding calculations, except accurate quantitative determinations, whole numbers will be used as the atomic weight.

number of atoms of the constituent elements in the molecule. From our knowledge of weight relationships, a formula then may express also a definite weight of matter, the gram-molecular weight. The relationship of formula, gram-molecular weight, and number of molecules for several substances is summarized in Table V.

Derivation of Formula. — Just as it was shown (Chapter IV) that potassium chlorate may be heated to give oxygen, so it may be determined quantitatively that a weighed amount of potassium chlorate will give a certain number of grams of oxygen. Further analysis will reveal to the chemist the number of grams of potassium and of chlorine in a sample of potassium chlorate. It is from such analyses that formulas are derived. The method is illustrated by the following calculation.

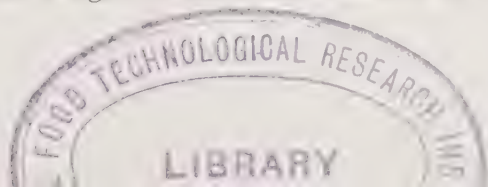
Problem: An analysis of potassium chlorate shows that the compound contains 31.97 per cent of potassium, 28.69 per cent of chlorine, and 39.34 per cent of oxygen. What is the formula for the compound?

Solution: The percentage composition of potassium chlorate expresses the part of each element in 100 parts of the compound. If each percentage is divided by the atomic weight of the corresponding element, the ratio of the gram-atomic weights is obtained:

$$\frac{31.97}{39} = 0.819 \quad \frac{28.69}{35} = 0.819 \quad \frac{39.34}{16} = 2.458$$

This calculation shows that in 100 grams of potassium chlorate, there are 0.819 gram-atomic weights of potassium, 0.819 gram-atomic weights of chlorine, and 2.458 gram-atomic weights of oxygen. Dividing each number by the common divisor (0.819) the ratio of elements becomes the whole numbers 1:1:3. In other words, potassium chlorate contains one atom of potassium, one atom of chlorine, and three atoms of oxygen, as shown by the formula KClO_3 .

Percentage Composition. — Having a formula with its corresponding gram-molecular weight, it is a simple matter to calcu-



late the percentage of each element in the compound. This is illustrated by the following problem: There are three oxides of iron with formulas FeO , Fe_2O_3 , and Fe_3O_4 . What is the percentage of iron in each oxide?

Calculation:

For FeO , the gram-molecular weight is $56 + 16 = 72$. The percentage of iron is $56/72 \times 100 = 77.8$ per cent.

For Fe_2O_3 , the gram-molecular weight is $(2 \times 56) + (3 \times 16) = 160$. The percentage of iron is $112/160 \times 100 = 70.0$ per cent.

For Fe_3O_4 , the gram-molecular weight is $(3 \times 56) + (4 \times 16) = 232$. The percentage of iron is $168/232 \times 100 = 72.4$ per cent.

Equations. — As stated in Chapter II, chemical reactions are represented by balanced equations. These equations now have a significance in terms of the weight of matter entering into reaction and the weight of matter in the product. The reaction of hydrogen with oxygen has been written in equation form:



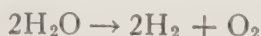
This may be read: Two gram-molecular weights of hydrogen (4 grams) combine with one gram-molecular weight of oxygen (32 grams) to form two gram-molecular weights of water or steam (36 grams). This is consistent with the law of conservation of matter (Chapter I), which states that in every chemical change, the total weight of matter entering into the reaction is equal to the total weight of matter in all the products. Moreover, this weight relationship explains the law of definite proportions, (Chapter II) which states that every pure compound is composed of a definite proportion by weight of its constituent elements. Since compounds can be formed from elements only in the proportion of their gram-molecular weights, as indicated by a balanced equation, any excess of either substance present must remain uncombined.

Problems. — It is evident that an equation represents a known and definite quantitative ratio between any two substances taking part in the chemical change. Using this known weight ratio

with a given weight of one of the substances, one may determine the weight of the other substance by arithmetic or by proportion. This is illustrated by several problems.

Problem: How many grams of water will be decomposed to form 15 grams of hydrogen?

Solution: The equation for the reaction is:



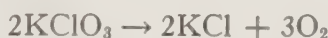
$$\frac{x \text{ g.}}{2(18)} = \frac{15 \text{ g.}}{4}$$

$$4x = 540$$

$$x = 135 \text{ g.}$$

Problem: How many grams of oxygen gas will be formed by heating 20 grams of potassium chlorate?

Solution:



$$\frac{20 \text{ g.}}{2(122)} = \frac{x \text{ g.}}{96}$$

$$244x = 1920$$

$$x = 7.8 \text{ g.}$$

The procedure for solving this type of problem may be summarized as follows:

- (1) Write and balance the equation for the reaction.
- (2) Write x grams under the unknown substance, and write the given amount, in grams, under the known substance. Under each of these write the gram-molecular weight.
- (3) Set up the proportion.
- (4) Solve the problem.

QUESTIONS AND PROBLEMS

1. What is the meaning of atomic weight? Tabulate the atomic weight and the molecular weight of the following elements: gold, hydrogen, iron, oxygen, nitrogen, and sodium. Explain why the molecular

- weight of hydrogen, oxygen, and nitrogen differs from the atomic weight.
- Define gram-molecular weight. Determine the gram-molecular weight of the following substances: carbon, oxygen, water, potassium chlorate. How many molecules are represented by the gram-molecular weight?
 - Define gram-atomic weight. What is the gram-atomic weight of carbon, oxygen, hydrogen?
 - Using the following expressions, tabulate the gram-molecular weight and the number of molecules corresponding to the weight represented: 2H_2 ; 5N_2 ; 2KClO_3 ; 3HgO ; 6Zn ; 4NH_3 .
 - Calculate the percent of nitrogen in compounds having the formulas: N_2O , NO , N_2O_3 , N_2O_5 , NO_2 .
 - Calculate the percentage of each element in the compounds: $\text{Ca}(\text{OH})_2$; ZnSO_4 .
 - Analysis of a compound shows 80.33 per cent zinc and 19.67 per cent oxygen. Derive the formula for the compound.
 - A compound contains 84.24 per cent of sulphur and 15.76 per cent of carbon. What is the formula for the compound?
 - How many grams of oxygen will be used in burning 40 grams of magnesium?
 - How many grams of hydrogen and of oxygen will be formed in the electrolysis of 150 grams of water? Using the weight of a liter of hydrogen and of oxygen, calculate each answer in liters.
 - How many grams of ferric oxide would be formed by the rusting (oxidation) of 30 grams of iron?
 - How many grams of oxygen will be formed when 150 grams of mercuric oxide are heated to decomposition?
 - How many grams of potassium chlorate will be needed to prepare 7.8 grams of oxygen?
 - How many grams of phosphorus pentoxide would form when 12 grams of phosphorus combine with oxygen?

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CHAPTER VI

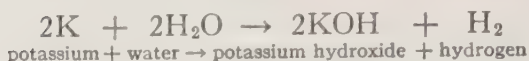
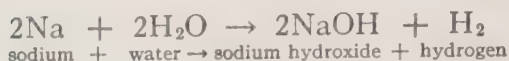
HYDROGEN. TYPES OF REACTION

NEXT to oxygen, the other constituent of water, hydrogen, is undoubtedly the most important element to study.

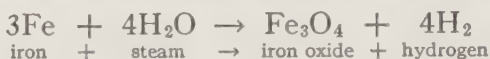
Occurrence. — As an element hydrogen is not found abundantly in nature, although it is present in natural gas, in the gases issuing from volcanoes, and in the gases surrounding the sun. It would make too long a list to mention all the known compounds containing hydrogen, but a few familiar ones will illustrate the importance of them. Hydrogen is present in all living matter and so it is a constituent of starch, sugar, protein, fats, and the cellulose or woody portion of plants. The constituents of petroleum — gasoline, kerosene, lubricating oils, vaseline, and paraffin — are compounds of hydrogen with carbon, called hydrocarbons. The sources from which hydrogen is most easily prepared are **water** and **acids**.

Preparation. — 1. *Electrolysis of Water.* The process of obtaining hydrogen gas and oxygen gas by electrolysis of water has been described (Chapter III). It is one of the most important of the methods used for commercial preparation of the element.

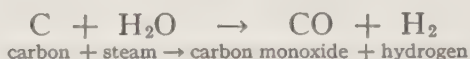
2. *Reaction of Water with a Metal.* Water, a compound, is decomposed and made to give up some of its hydrogen by reaction with certain metals. Of the metals familiar to us, sodium and potassium react most vigorously; magnesium, zinc, and iron come next in order; while copper, gold, and platinum do not react with water at all. With potassium the reaction is rapid and furnishes sufficient heat to make the hydrogen gas burn spontaneously as it appears at the surface of the water. The reactions of sodium and potassium with water may be written as follows:



Magnesium reacts with hot water, while zinc and iron react only when steam is passed over the heated metal.¹ This latter reaction is useful in the preparation of hydrogen gas for commercial use. Steam is passed through a tube containing heated iron, and hydrogen gas is formed according to the reaction:



3. *Reaction of Water with the Non-Metal Carbon.* Hydrogen gas is one of the products formed by passing steam over red-hot coke (carbon). The reaction occurs as follows:



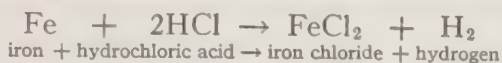
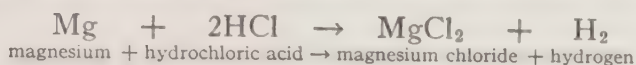
This reaction forms two gases both of which burn with a very hot flame. Thus the reaction is valuable for the preparation of a fuel gas as well as for the preparation of hydrogen for commercial use.

4. *Reaction of a Metal with Dilute Acid.* Acids are compounds containing hydrogen combined with other elements in such a way that the hydrogen is easily displaced by metals. The very active metals, such as sodium and potassium, which displace hydrogen readily from water, react too vigorously with acid to make their use practicable. Magnesium, zinc, iron, and aluminium easily displace hydrogen from acids. They are therefore often used in the laboratory preparation of the gas. Copper, mercury, silver, gold, and platinum are not active as metals, and hence do not react with dilute acids to displace hydrogen.

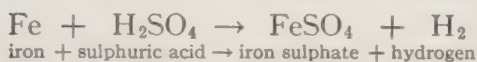
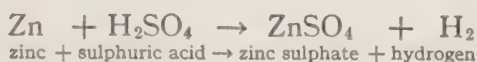
Hydrochloric acid is a water solution of hydrogen chloride, HCl, a compound containing hydrogen and chlorine. When a

¹ It should be noted that similar reactions cause an oxide or rust to form upon the surface of such metals as zinc or iron. When food is cooked in iron utensils of an older type, there is some reaction of the steam on the iron to form iron oxide; at the present time, iron is made into stainless steel utensils, treated in such a way that steam does not react with the iron.

metal reacts with this acid, the metal combines with the chlorine to form a binary compound (a chloride), and the hydrogen gas is liberated. The following equations illustrate this reaction:



Sulphuric acid is a water solution of hydrogen sulphate H_2SO_4 , a compound containing hydrogen, sulphur, and oxygen. When certain metals react with this acid, the hydrogen is displaced and a sulphate is formed. Equations for typical reactions are as follows:



Reactions of this type are called **displacements**. In this case the metal displaces the hydrogen of the acid. When these reactions take place in the laboratory (Fig. 6), the hydrogen escapes as a gas and the compound formed is not seen because it is dissolved in the water.

In the preceding paragraphs the metals are classified as active, less active, and inactive. All the metals and hydrogen have been arranged in the form of a table showing the order of reactivity. This table, called the activity series or the **electrochemical series**, is given in the appendix, and is explained more fully in Chapter XIV. It is sufficient for the present to know that in the electrochemical series, all the metals above hydrogen will displace it from dilute acids. The most reactive elements at the head of the series will displace hydrogen from water. Metals below hydrogen are comparatively inactive and are not acted upon by dilute acids. Thus it is evident that we must choose carefully the metal to react with the acid in the preparation of hydrogen gas.

Choice of Method. — In Chapter IV it was suggested that the choice of method for the preparation of any substance depends on

the amount needed and the convenience of obtaining the source material. The best laboratory method for preparing hydrogen is the rapid and simple reaction of a metal with an acid. The apparatus used is shown in Figure 6 and is described fully in the laboratory manual.

In order to make available a small amount of hydrogen gas, needed for lecture demonstration or other work, the Kipp generator, shown in Figure 7, is often used. The metal is placed in the central compartment B, and the acid is added through C, which extends through the center of the apparatus into A. When

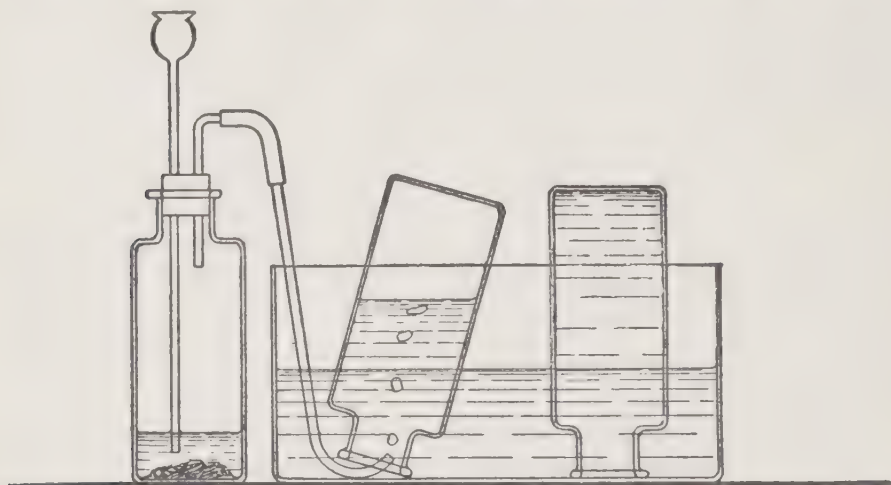


FIG. 6. Preparation of Hydrogen

the generator is in operation and the stop-cock D is opened, the gas in B escapes, permitting the acid to rise from A into B so that it may come in contact with the metal. Hydrogen gas may be obtained at the exit tube as long as needed. On the closing of the stop-cock D, there is no escape for the hydrogen gas, so its pressure forces the acid back into C and hence the reaction ceases until the stop-cock is again opened.

When hydrogen gas is needed in large amounts for balloons, for the oxyhydrogen blowpipe, or for any other commercial use, acids are too expensive as a source of hydrogen. Water is used as the source material, and hydrogen is obtained from it by electroly-

sis or by passing steam over hot coke or heated iron. The hydrogen is compressed in metal tanks and shipped wherever needed. The tanks are provided with valves allowing the hydrogen to be obtained conveniently (Fig. 8).

Properties of Hydrogen. — *Physical.* Hydrogen is the lightest known gas; it is only one sixteenth as heavy as oxygen. At the same temperature and pressure, one liter of hydrogen gas weighs 0.0898 g. while one liter of oxygen gas weighs 1.429 g. Hydrogen gas is colorless, odorless, tasteless, and only slightly soluble in water. In the laboratory hydrogen is collected in gas-bottles by displacement of water. When removed from the water, the bottles are kept in an inverted position because hydrogen is so light that it would escape from a bottle standing upright even though it were covered. Finely divided metals, such as platinum, silver, and palladium, absorb or dissolve hydrogen in the mass of metal. This absorbed or "occluded" hydrogen is chemically very active and combines readily with other elements. In this way the finely divided metal may act as a catalytic agent, facilitating the combination of hydrogen with other gases.

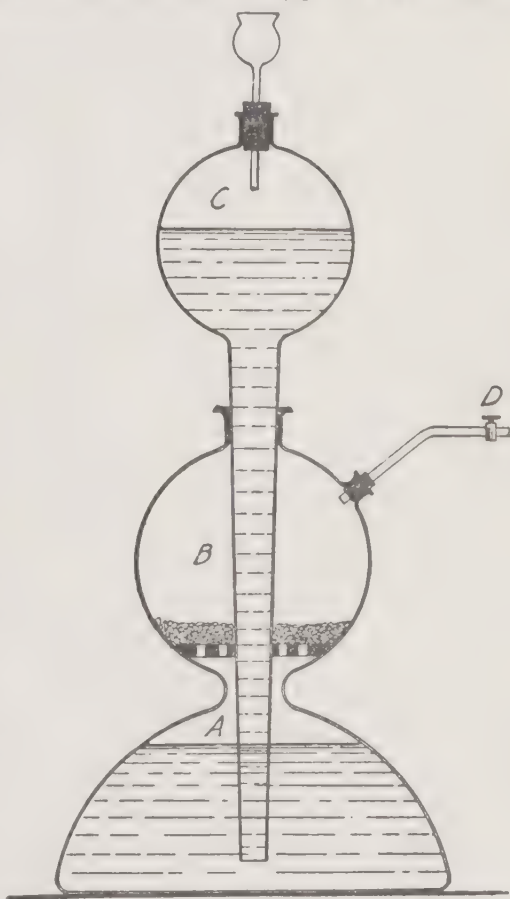


FIG. 7. Kipp Generator

Because of its lifting power, hydrogen is used for inflating dirigibles and balloons. There is a serious disadvantage, however, because of the ease with which hydrogen burns. Many will remember the disastrous burning of the hydrogen-filled dirigible, Hindenburg. Helium gas, which does not burn, is used instead of hydrogen in American dirigibles.

2. *Chemical.* Hydrogen and oxygen gases may be mixed at ordinary temperatures without the occurrence of any chemical

change. As the mixture is heated, the gases react slowly to form water vapor, but at 700°C . and above the gases combine with explosive violence. In preparing hydrogen in the laboratory, the first gas collected from a generator bottle is an explosive mixture of air and hydrogen. Since a lighted Bunsen burner may furnish enough heat to explode this mixture, the apparatus must be kept away from the flame. In the preparation of hydrogen and the study of its properties, all directions must be followed carefully. Pure hydrogen gas may be ignited as it issues from a glass jet attached to the exit tube of the generator bottle. The number of calories of heat evolved in the burning of one gram of hydrogen is greater than that obtained when one gram of wood or coal is burned. We make use of the heat of combustion of hydrogen when we burn natural gas or commercial gas, both of which contain hydrogen. The oxyhydrogen blowpipe is a device in which



FIG. 8. Hydrogen Tank

hydrogen is burned in pure oxygen, making a flame so hot that it can cut through a bar of iron or melt platinum.

A **test for hydrogen** is made by inserting a burning splint in a bottle of gas. Hydrogen gas smothers the flame of the splint but at the mouth of the bottle, the hydrogen gas ignites as it comes in

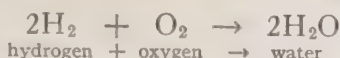


Courtesy of Pictures, Inc. (from the Philadelphia Public Ledger)

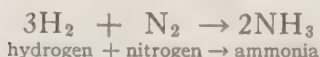
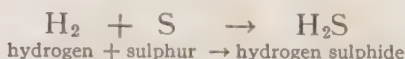
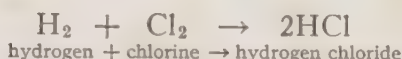
BURNING OF THE *Hindenburg*

In May, 1937, the *Hindenburg*, a dirigible filled with hydrogen gas, which had made ten round trips from Germany to the United States and was considered one of the safest means of transport, suddenly caught fire as it landed at Lakehurst, New Jersey. The flames shot 500 feet into the air, and in 32 seconds the dirigible had burned completely. The *Hindenburg* was filled with hydrogen gas. Had the dirigible been filled with helium, it would not have burned. The cost of helium is many times that of hydrogen, and helium has not quite the lifting power of hydrogen. However, this accident proved beyond any doubt the importance of using the non-inflammable gas, helium, for filling dirigibles.

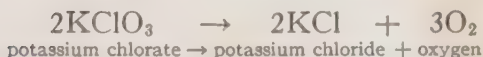
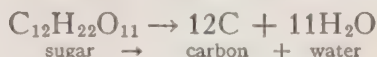
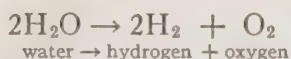
contact with the oxygen of the air. The equation which illustrates this reaction follows:



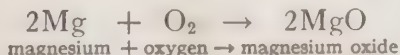
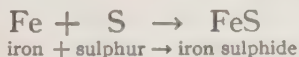
At high temperatures or with a catalyst, hydrogen will unite with several non-metals. The following equations illustrate the reactions:



Types of Reactions. — The many changes which occur in the study of chemistry will not appear to be so confusing if they can be classified or grouped. The reactions so far studied may be classified as follows: (1) **Decomposition**, a reaction in which a compound is separated into its elements or into simpler substances. The following reactions are illustrative of this type:

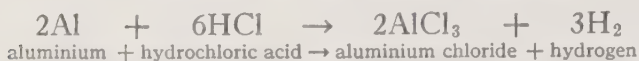
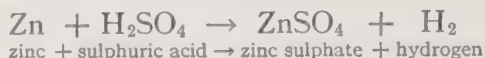


(2) **Combination**, a reaction in which a compound is formed by direct union of elements. The following reactions are illustrative of this type:



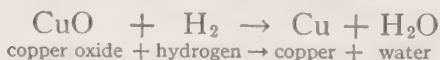
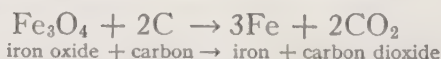
(3) **Displacement**, a reaction in which an element pushes out or liberates a less active element from a compound. In the following

equations, zinc liberates hydrogen from sulphuric acid and aluminium liberates hydrogen from hydrochloric acid.



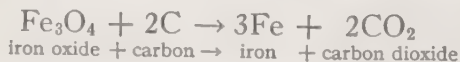
All reactions involve a change in energy and so may be grouped as follows: (1) **Exothermic** reactions, in which heat is evolved during the reaction. The burning of hydrogen, wood, or coal illustrates an exothermic reaction. (2) **Endothermic** reactions, in which heat is absorbed by the chemical change. The heating of potassium chlorate or of mercuric oxide to obtain oxygen and the decomposition of sugar by heat are illustrative of endothermic reactions.

Many reactions, some of them included in the foregoing paragraph, are of the **oxidation-reduction** type. For the present, these may be designated as those causing a change in the oxygen content of the original matter. A few examples follow:



In its simplest interpretation, **oxidation** has been defined as a reaction in which oxygen combines with another element. In a **reduction** reaction, an element takes oxygen from a compound. In the preceding examples, the oxidizing agent (iron oxide or copper oxide) furnishes the oxygen, and the reducing agent (hydrogen or carbon) combines with the oxygen. Other oxidizing agents and reducing agents will be studied in later chapters.

The name oxidation-reduction signifies that the two processes occur in the same reaction. An analysis of one of the preceding reactions bears out this statement; for example, in the reaction:



the process of oxidation is illustrated by the union of carbon with oxygen to form carbon dioxide, while the process of reduction is

shown when the iron oxide gives up the oxygen to the carbon and iron is formed as a product. Commercially, iron oxide ore is made into the element iron by an oxidation-reduction reaction of the type illustrated. Similar reactions are used for the preparation of other elements from compounds occurring in nature.

Summary of Formulas. — The equations for the preparation and properties of hydrogen gas involve formulas for several compounds which have been studied in the laboratory. A few examples follow:

NaOH	sodium hydroxide
KOH	potassium hydroxide
CO	carbon monoxide
MgCl ₂	magnesium chloride
FeCl ₂	iron chloride (ferrous chloride)
ZnSO ₄	zinc sulphate
FeSO ₄	iron sulphate (ferrous sulphate)
HCl	hydrochloric acid or hydrogen chloride
H ₂ SO ₄	sulphuric acid
H ₂ S	hydrogen sulphide
NH ₃	ammonia
AlCl ₃	aluminium chloride
CuO	copper oxide
FeS	iron sulphide (ferrous sulphide)

QUESTIONS AND PROBLEMS

1. From what compound is hydrogen gas obtained commercially? Write equations for the reactions used in preparing hydrogen gas by (1) electrolysis of water, (2) steam with iron, (3) steam with carbon.
2. Diagram the apparatus used in the laboratory for the preparation of hydrogen gas. What materials are used in making hydrogen? What compound is the source of the hydrogen?
3. Diagram and explain the Kipp generator as it is used in making hydrogen gas.
4. Write an equation to show the reaction of sodium with water; of potassium with water.
5. Name five metals that may be used to liberate hydrogen gas from an acid. Name two metals that are not sufficiently reactive to displace hydrogen from acids.

6. Choose from the following list the reactions that will occur (use electrochemical series), and write equation for each successful reaction:
- zinc with sulphuric acid
 - iron with sulphuric acid
 - copper with hydrochloric acid
 - aluminium with hydrochloric acid
 - iron with hydrochloric acid
 - silver with hydrochloric acid
 - magnesium with hydrochloric acid.
7. Give two commercial uses of hydrogen gas. What properties are advantageous and what properties are disadvantageous for each use?
8. Write equations for the combination reactions that occur with hydrogen and chlorine, hydrogen and sulphur, hydrogen and nitrogen.
9. From the methods used in laboratory experiments, classify the following reactions as exothermic or endothermic:
- decomposition of sugar
 - decomposition of mercuric oxide
 - decomposition of potassium chlorate
 - electrolysis of water
 - burning hydrogen
 - burning magnesium
 - burning carbon
 - burning sulphur
 - zinc with sulphuric acid.
10. Write three equations to illustrate oxidation-reduction. In each equation, indicate the substance oxidized, the substance reduced, the reducing agent, the oxidizing agent.
11. Write and balance the following equations:
- ferrous sulphide + hydrochloric acid \rightarrow ferrous chloride + hydrogen sulphide
 - magnesium + steam \rightarrow magnesium oxide + hydrogen
 - ferrous chloride + sulphuric acid \rightarrow ferrous sulphate + hydrogen chloride
 - sulphuric acid + carbon \rightarrow carbon dioxide + sulphur dioxide + water
 - aluminium + chlorine \rightarrow aluminium chloride
12. How many grams of hydrogen would be obtained by the reaction of 10 g. of zinc with sulphuric acid? Using the weight of one liter of hydrogen, calculate the number of liters of hydrogen obtained.
13. Diagram the apparatus used in the laboratory for reduction of copper oxide with hydrogen. Calculate the number of grams of copper formed by reaction of hydrogen with 12 grams of copper oxide.
14. How many grams of carbon would be required to reduce 8 kilograms of iron oxide (Fe_3O_4)?

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CHAPTER VII

ATOMIC STRUCTURE AND VALENCE

THE equations which have been written in the previous chapters show molecules in action; for example, the equation



tells us that when sugar undergoes a chemical change, the molecules of sugar are decomposed, and the atoms that are released from the sugar rearrange themselves to form molecules of carbon and molecules of water. Thus the atom is the building unit through which molecules of one kind are made into molecules of another kind.

It was in 1803 that John Dalton, an English schoolmaster, devised the earliest theory of atoms. He believed that molecules and thus all kinds of matter are composed of atoms, that atoms of each element are made of material different from that of any other kind of atoms, that each kind of atom has a definite weight different from all other atoms, and that chemical change takes place between atoms. This conception of atoms did much to clarify the early chemists' idea of the nature of matter, but more recent experiments have modified it.

According to the theory devised by Dalton, atoms were conceived to be stable impenetrable particles of matter. He considered that there was no possibility of changing the atoms of one kind of element into those of another kind. This ended definitely the attempts of early alchemists to make gold from baser metals. Between 1896 and 1900, however, the French scientists Becquerel, Pierre Curie, and Marie Curie discovered the property of radioactivity in elements with complex atoms, such as uranium and radium. Atoms of these elements were shown to disintegrate spontaneously into elements whose atoms were simpler in structure. Some of the particles emitted during the disintegration

had positive charges of electricity and others had negative charges. These electrically charged particles were actually a structural part of the atom. More recently, scientists have been able to change atoms of several elements into other kinds of atoms, and to cause at least fifty different elements to become temporarily radioactive. These and other experiments have demonstrated without doubt that all atoms are related in structure and are composed of units that are electrical in nature.

Electronic Structure of the Atom. — A brief outline of the theory of atomic structure as it is taught to-day will be helpful in understanding the chemical properties of elements and the part that atoms play in the formation of compounds. Later, in Chapter XXI, a more nearly complete picture of atomic structure will be given. Scientists believe that atoms are composed of three distinct fundamental units known as **electrons**, **protons**, and **neutrons**. The electron is the unit of negative electricity and will exactly neutralize a proton, which is the unit of positive electricity. The neutrons are electrically neutral and are considered to be a proton and an electron closely bound together. The weight of the neutron is the same as the weight of the proton and practically the same as the weight of the hydrogen atom. The weight of the electron is only $1/1,845$ that of the proton, neutron, and hydrogen atoms and so is considered negligible when compared to them.

The atoms of the element hydrogen are the simplest of all the ninety-two kinds of atoms. The hydrogen atom consists of a proton with an electron revolving about it in an orbit or elliptical path (Fig. 9). When the hydrogen atom enters into a chemical reaction, the electron may leave its orbit entirely and the atom then becomes merely a proton, or positive electric charge. It is often represented as H^+ , and is called a **hydrogen ion**.



FIG. 9. Hydrogen

Other atoms are more complex, but similar in structure. In these other atoms both protons and neutrons are clustered tightly together in a nucleus, while the electrons, which are so

much lighter, revolve about this nucleus in one or more orbits at different distances from the nucleus. They are said to form a planetary system. The diagrams in the text illustrate the orbits in

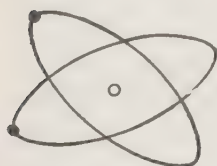


FIG. 10. Helium

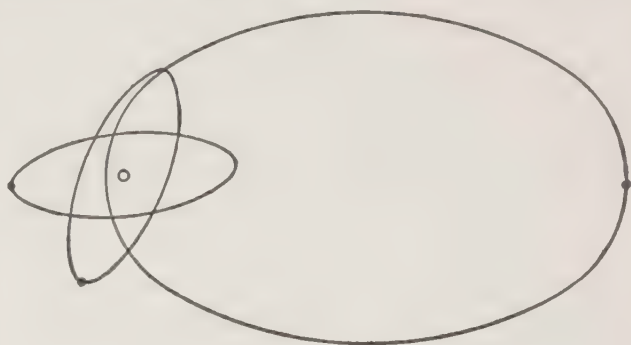


FIG. 11. Lithium

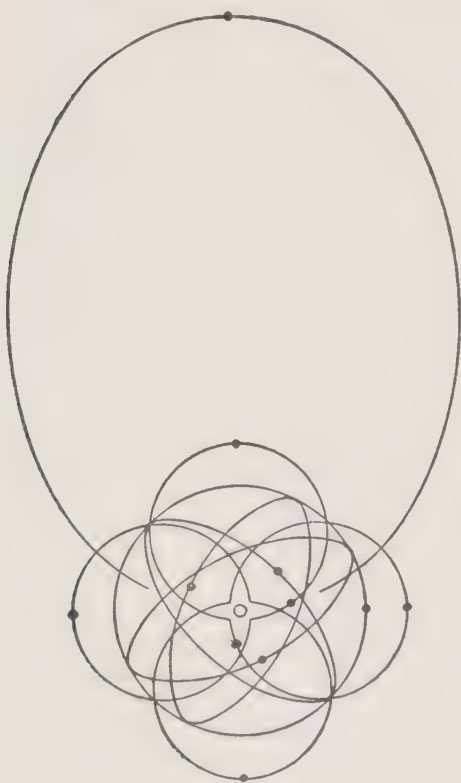


FIG. 12. Sodium

which the electrons move, while the tiny circle in each diagram represents the combination of protons and neutrons that form the nucleus.

Next to the hydrogen atom, the atom of the element helium is simplest in structure. The nucleus of the helium atom contains both protons and neutrons, and there are two electrons that revolve about this nucleus as shown in Figure 10. Note that both electrons move in orbits that are equally distant from the nucleus. In lithium atoms (Fig. 11), on the other hand, there are three electrons revolving about the nucleus, two in an orbit similar to that

of helium, and a third in an orbit that is much farther from the nucleus. This outside electron may be readily dislodged from its orbit. The sodium atom (Fig. 12) is much more complex and is drawn on a smaller scale. It has two of its eleven electrons moving in an orbit similar to that of helium or the first orbit of lithium. In an orbit similar to the second orbit of lithium it has eight electrons, while the eleventh electron is in an orbit by itself and much larger than the others. Study the diagrams and the comparative structures of these four atoms until they are familiar.

The relationship of neutrons, protons, and electrons may be shown in another type of diagram represented in Figure 13. (See also Table XVIII, Chapter XXI.) In these diagrams, the neutrons are shown as \pm (a proton and electron held together) and the number of free protons in the nucleus of the atom is equal to the number of electrons outside the nucleus. Consequently the uncombined atoms have zero charge.



FIG. 13. Structure of Some Atoms

Atomic Structure and Chemical Change. — We have shown in the preceding paragraph that atoms differ with regard to the number of neutrons and protons in the nucleus, and the number of electrons outside the nucleus. Actually, the chemical properties of an element are almost entirely dependent on the number of electrons in the outside orbit of its atom. Atoms of all elements have a similar characteristic structure, but they differ by having one, two, three, four, five, six, seven, or eight electrons in the outside orbit. Experiments have shown that helium with two electrons traveling in one orbit and also elements having eight electrons in the outer orbit are inert, inactive elements. They do

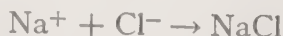
not combine with other elements or enter into any chemical changes; thus it appears that these atoms have a stable structure. When other elements enter into chemical change, there is either a transfer of the electrons of the outer orbit from one atom to another, or electrons are shared by both kinds of atoms that take part in the reaction.

We have learned that the atoms of sodium and lithium, with zero electric charge, each have one electron in an outer orbit far from all other electrons. Atoms of this type have a tendency to transfer the outside electron to other atoms. They are then left with an excess of one positive charge. In this form they are known as **ions** and are written Na^+ , sodium ion, and Li^+ , lithium ion. Other atoms, for example magnesium, have two electrons in their outer orbits. These atoms have a tendency to transfer the two electrons and form ions with two excess positive charges, such as Mg^{++} , magnesium ion.

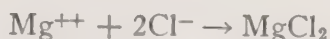
Chlorine atoms have seven electrons and sulphur atoms have six electrons in the outer orbit. Elements of this type have a tendency to add enough electrons to make a total of eight in their outer orbits. Since they are neutral before adding these electrons, they acquire an excess negative charge of one or two. Thus chlorine atoms become chloride ions, Cl^- , with one excess negative charge, while sulphur atoms become sulphide ions, $\text{S}^{=}$, with two excess negative charges.

Ions are very different from the atoms from which they are derived. The element chlorine is an extremely poisonous yellow gas, but when chlorine atoms acquire an electron and become chloride ions they are harmless and even beneficial to the body. In a similar way, sodium atoms are very reactive, but as sodium ions, Na^+ , they are stable and hard to change.

The compound sodium chloride forms when sodium ions having one positive charge come in contact with chloride ions that have one negative charge. Since the charges upon these ions are equal but of opposite sign, the molecule, NaCl , is electrically neutral. This may be written:



When magnesium chloride forms from magnesium and chloride ions, the compound has the formula MgCl_2 . Magnesium ion, Mg^{++} has two positive charges, and chloride ion has one negative charge. Therefore, two chloride ions are needed with one magnesium ion to make the neutral molecule MgCl_2 , as shown by the following:



The formula MgCl_2 is determined by the charge of the ions that make up the compound.

Thus far we have not considered any atoms with from three to five electrons in their outer orbits. Elements with three electrons act in a way similar to those with one or two electrons and have a tendency to give up these three electrons and form ions with three positive charges. However, instead of transferring the electrons, the tendency is stronger to share the electrons equally with other atoms. Elements with four or five electrons in their outer orbit almost always share electrons with other atoms in such a way that each element has a complete orbit of eight electrons.

Valence. — The capacity of an atom of an element to give off, take on, or share electrons is called the **valence** of the element. As we have shown in the formation of sodium chloride and magnesium chloride, *valence determines the formulas for the compounds formed by the elements.*

The relationship between valence and the structure of the atom may be summarized as follows: All uncombined elements have zero electric charge or zero valence because they have equal numbers of protons and electrons. Ions having a positive valence contain more protons than electrons. They are known as **positive ions**, such as Na^+ , Mg^{++} . Ions having a negative valence contain more electrons than protons. They are known as **negative ions**, such as Cl^- , $\text{S}^{=}$. Elements that share electrons do not form true ions but still have a definite valence that is dependent on the number of electrons that must be shared to complete their outer orbits to a total of eight electrons.

To Derive Valence from a Formula. — In Table VI formulas are given for compounds containing the elements for which the valence is indicated. We may use a formula to derive the valence of an element in a binary compound if we know the valence of one of the two elements. The principle involved is that every molecule is electrically neutral, or the sum of the positive charges is equal to the sum of the negative charges. For example, if it is known that AlCl_3 is a correct formula and that the valence of the chloride ion, Cl^- , is a negative one, it is possible to determine the valence of the aluminium ion. The three chloride ions have a total charge of negative three; therefore, the positive charge of one aluminium ion is three, Al^{+++} . To remember valence, then, one may either associate a number, positive or negative, with each atom (Table VI) or one may remember a typical formula for each element and derive the valence.

TABLE VI

VALENCE

Hydrogen and metals have a tendency to transfer electrons to other atoms, and so they form positive ions, as shown by the following valences and typical formulas:

<i>Element</i>	<i>Typical Formula</i>	<i>Valence</i>
Hydrogen	HCl	H^+
Sodium	NaCl	Na^+
Potassium	KCl	K^+
Silver	AgCl	Ag^+
Zinc	ZnCl_2	Zn^{++}
Copper	CuCl_2	Cu^{++}
Calcium	CaCl_2	Ca^{++}
Barium	BaCl_2	Ba^{++}
Mercury	HgCl_2	Hg^{++}
Magnesium	MgCl_2	Mg^{++}
Iron	FeCl_2	Fe^{++}
	FeCl_3	Fe^{+++}
Aluminium	AlCl_3	Al^{+++}

Elements (non-metals) that unite with hydrogen or metals either by sharing or by transfer of electrons have an apparent negative valence as shown by the following formulas:

<i>Element</i>	<i>Typical Formula</i>	<i>Valence (negative)</i>
Chlorine	HCl	Cl (1)
Iodine	HI	I (1)
Bromine	HBr	Br (1)
Sulphur	H ₂ S	S (2)
Oxygen	H ₂ O	O (2)
Nitrogen	NH ₃	N (3)
Phosphorus	PH ₃	P (3)
Carbon	CH ₄	C (4)

Elements (non-metals) that unite with oxygen either by sharing or by transfer of electrons have an apparent positive valence as shown by the following formulas (the most characteristic valences are indicated):

<i>Element</i>	<i>Typical Formula</i>	<i>Valence (positive)</i>
Sulphur	SO ₂	S (4)
	SO ₃	S (6)
Nitrogen	N ₂ O ₃	N (3)
	N ₂ O ₅	N (5)
Phosphorus	P ₂ O ₃	P (3)
	P ₂ O ₅	P (5)
Carbon	CO ₂	C (4)

Radicals. — A **radical** consists of a group of atoms that acts in most chemical reactions as a single unit with a characteristic valence. We may note that in the compounds H₂SO₄, ZnSO₄, and MgSO₄ the radical or group of atoms SO₄ is the same in each compound. The valence of a radical may be determined just as in binary compounds, from a correct formula containing the radical; thus from the formula H₂SO₄ we know that two hydrogen ions have a total charge of positive two. These must be balanced by a charge of negative two, which is then the valence of the sulphate ion, SO₄⁼. In sodium hydroxide NaOH, the hydroxide radical OH⁻ is an ion with a valence of negative one. Potassium chlorate, KClO₃, contains the chlorate radical, ClO₃, an ion with a valence of negative one. In ammonium chloride, NH₄Cl, the ammonium radical NH₄⁺ is an ion with a valence of positive one.

Many other radicals will be studied in later chapters. The following radicals with their charge should be kept in mind:

$\text{SO}_4^{=}$	sulphate, negative two
ClO_3^{-}	chlorate, negative one
OH^{-}	hydroxide, negative one
NH_4^{+}	ammonium, positive one.

To Derive a Formula (Knowing the Valence of Ions). — In the valence table and the explanation following it, we have indicated that the formula for a compound depends upon the valence of the constituent ions. This is true whether the ion is that of an element, such as sodium ion, Na^{+} , or of a radical, such as sulphate ion, $\text{SO}_4^{=}$. The formula for a compound is determined by using the number of ions of each kind (as a subscript) which is required to make the sum of the positive valences equal to the sum of the negative valences. A few examples follow:

Mg^{++}	with I^{-} forms MgI_2 , magnesium iodide
Zn^{++}	with $\text{S}^{=}$ forms ZnS , zinc sulphide
Na^{+}	with $\text{SO}_4^{=}$ forms Na_2SO_4 , sodium sulphate
NH_4^{+}	with OH^{-} forms NH_4OH , ammonium hydroxide
Mg^{++}	with $\text{N}^{=}$ forms Mg_3N_2 , magnesium nitride.

Variable Valence. — It may be noted in the table of valences that iron ions have either two or three positive charges. This indicates that iron atoms may give up either two or three of the electrons of the outer orbit. Many other elements will be encountered that may have more than one characteristic valence. In order to distinguish between the two types of compounds, those in which iron has a valence of two are called **ferrous compounds**, while those in which iron has a valence of three are called **ferric compounds**; for example, FeCl_2 is ferrous chloride and FeCl_3 is ferric chloride. This nomenclature is consistently used in compounds in which other elements have two valences, *-ous* signifying the lower valence and *-ic* signifying the higher valence.

The valence table indicates that carbon, nitrogen, phosphorus, and sulphur also have variable valence. These elements with four, five, and six valence electrons (electrons in the outer orbit of

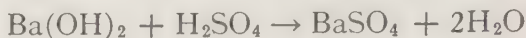
their atoms) have little tendency to give up or to lose electrons and almost always share them with other atoms. However, we still may consider that they have a positive or negative valence or combining power. Thus, when nitrogen combines with elements that are electro-positive (form positive ions), the compounds have formulas such as NH_3 , Na_3N , and Ca_3N_2 . If these compounds are electrically neutral, the nitrogen must have a possible combining power equivalent to three negative charges. In a similar way, when nitrogen combines with an electro-negative ion it appears to have a valence equivalent to three or five positive charges, as in N_2O_3 and N_2O_5 . A more detailed explanation of the electron changes in these compounds will be found in Chapter XII. When a non-metal, such as nitrogen, forms two or more compounds with another element, it is customary to distinguish between them by using a prefix to denote the number of atoms combined; for example, N_2O_3 is nitrogen trioxide and N_2O_5 is nitrogen pentoxide.

Double Decomposition Reactions. — In Chapter IV, reactions were classified to include three types — combination, decomposition, and displacement. A fourth type of reaction, **double decomposition**, occurs when two compounds enter into reaction. In reactions of this type, the positively charged elements or radicals of one compound react with the negatively charged elements or radicals of the other compound — an interchange of ions. For example, when ferrous sulphide and hydrogen chloride react, the positive ferrous ions, Fe^{++} , react with negative chloride ions, Cl^- , to form ferrous chloride, FeCl_2 , and positive hydrogen ions, H^+ , react with negative sulphur ions, $\text{S}^{=}$, to form hydrogen sulphide gas, H_2S . The following equation represents the reaction:



Radicals enter into these reactions as a unit having a characteristic valence. When barium hydroxide, $\text{Ba}(\text{OH})_2$, reacts with sulphuric acid, H_2SO_4 , barium ion, Ba^{++} , combines with sulphate ion, $\text{SO}_4^{=}$, to form barium sulphate, BaSO_4 , and two hydrogen

ions, 2H^+ , combine with two hydroxyl ions, 2OH^- , to form two molecules of water. The equation is shown as follows:



This type of reaction is known as double decomposition because both compounds entering into the reaction are decomposed, and two new compounds are formed. A further discussion of these reactions will be found in Chapter XIV.

QUESTIONS AND PROBLEMS

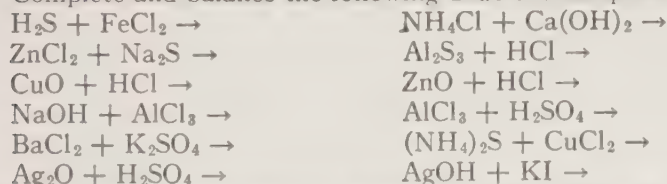
1. Explain the structure of the atom in terms of electrical units. How does this conception of the atom differ from that formulated by John Dalton? How did the work of Pierre and Marie Curie furnish evidence that the electron conception is correct?
2. Describe the structure of the atom of helium; of lithium. Explain the weight of the neutron, proton, and electron. What is the electrical charge of each?
3. Why is the number of electrons in the outside orbit an important characteristic of an atom? Illustrate by explaining the charge acquired by atoms of sodium when they enter into chemical change. Explain the charge acquired by magnesium.
4. What is an ion? Explain the difference in the structure of sodium atoms and sodium ions. Compare the properties of each.
5. Define valence. How do we use valence?
6. How do neutral atoms become ions with a positive charge? What is the positive valence of the ions formed by the following elements:
 calcium, two electrons in outer orbit
 potassium, one electron in outer orbit
 aluminium, three electrons in outer orbit
 tin, four electrons in outer orbit
7. How do neutral atoms become ions with a negative charge? What is the negative valence of the ions formed by the following elements:
 nitrogen, five electrons in outer orbit
 sulphur, six electrons in outer orbit
8. From the fact that hydrogen has a valence of $+1$ and oxygen a valence of -2 , and that each molecule must be neutral, determine the valence of each atom in the following formulas: MnO_2 , Mn_2O_7 , VH_3 , WO_3 , Sb_2O_3 , SnO_2 , As_2O_5 , Bi_2O_3 , SiH_4 , H_2Te , HBr , RaBr_2 , AgBr , HNO_3 .
9. What is a radical? From the following correct formulas determine the valence of the underlined radicals: $\text{H}_3\underline{\text{PO}_4}$, $\text{H}\underline{\text{NO}_3}$, $\text{Ag}\underline{\text{OH}}$, $\text{Na}_2\underline{\text{B}_4\text{O}_7}$, $(\underline{\text{NH}_4})_3\text{PO}_4$.

10. Using the valences given in the table in the text write formulas for the compounds:

sodium oxide	barium oxide	aluminium oxide
sodium chloride	barium chloride	aluminium chloride
sodium sulphide	barium sulphide	aluminium sulphide
sodium nitride	barium nitride	aluminium nitride
sodium iodide	barium iodide	aluminium iodide
sodium hydroxide	barium hydroxide	aluminium hydroxide
sodium sulphate	barium sulphate	aluminium sulphate
sodium chlorate	barium chlorate	aluminium carbide
copper oxide	zinc iodide	mercury iodide
ammonium sulphide	copper sulphate	silver sulphide
ammonium sulphate	magnesium nitride	potassium sulphate
ferric oxide	calcium oxide	magnesium hydroxide
ferrous hydroxide	ferrous chloride	calcium chlorate

11. Considering the valence of oxygen as -2 and that of hydrogen as $+1$, give the valence of the other elements in the following compounds: H_2S , SO_2 , SO_3 , N_2O , NO , N_2O_3 , NO_2 , N_2O_5 , NH_3 , P_2O_3 , P_2O_5 , PH_3 .

12. Complete and balance the following double decomposition equations:



13. Using correct formulas write equations for the following:

zinc oxide with sulphuric acid
 ferrous sulfide with hydrochloric acid
 sodium iodide with silver sulphate
 potassium sulphate with barium chloride
 aluminium chloride with ammonium hydroxide
 silver sulphate with ammonium chloride
 ammonium sulphide with copper sulphate
 barium hydroxide with ferric chloride
 mercury sulphate with potassium hydroxide

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CHAPTER VIII

CHARACTERISTICS OF GASES, LIQUIDS, AND SOLIDS GAS LAWS—MOLECULAR THEORY

Introduction. — We think of iron as a solid, of water as a liquid, and of carbon dioxide as a gas because it is in these physical states that each is known at ordinary temperature and pressure. It is a familiar fact, however, that water may be frozen to a solid or evaporated to a gas and that iron may be turned into a melted mass, or even a vapor, by application of sufficient heat. Carbon dioxide is evolved in the gaseous condition when baking powder reacts or when the pressure on a carbonated beverage is released. Carbon dioxide is known also in the liquid and the solid states. As a solid it is the dry ice so convenient for refrigeration. Experiments have shown that it is possible to make many substances assume each of the three physical states.

Gases always expand to fill completely any containing vessel. This property distinguishes gases from liquids and solids. A drop of perfume as it changes to a gas may be detected in any part of a room; if part of the air is removed from a vessel, the remaining air will expand to fill the container; one can compress many volumes of gas into an automobile tire. From these statements, it is evident that a given volume may contain a much more variable weight of gas than of a solid or liquid. If we had to buy a quart of air, as we buy a quart of milk, some standard weight of air would have to be designated as filling the volume. It will be seen that pressure and temperature are the most important factors in determining the weight of a certain gas which fills a given volume.

THE GAS LAWS

Relationship of Volume to Temperature. — “Heat expands and cold contracts” is a general statement (to which there are exceptions) that must be realized concerning solids, liquids, or gases.

Stoves, kettles, thermometers, and all metal appliances are built on this principle. Stove lids and kettle covers are made to fit loosely when cold; when heated, the expansion of the metal makes them fit more closely. If one liter of boiling water is cooled to

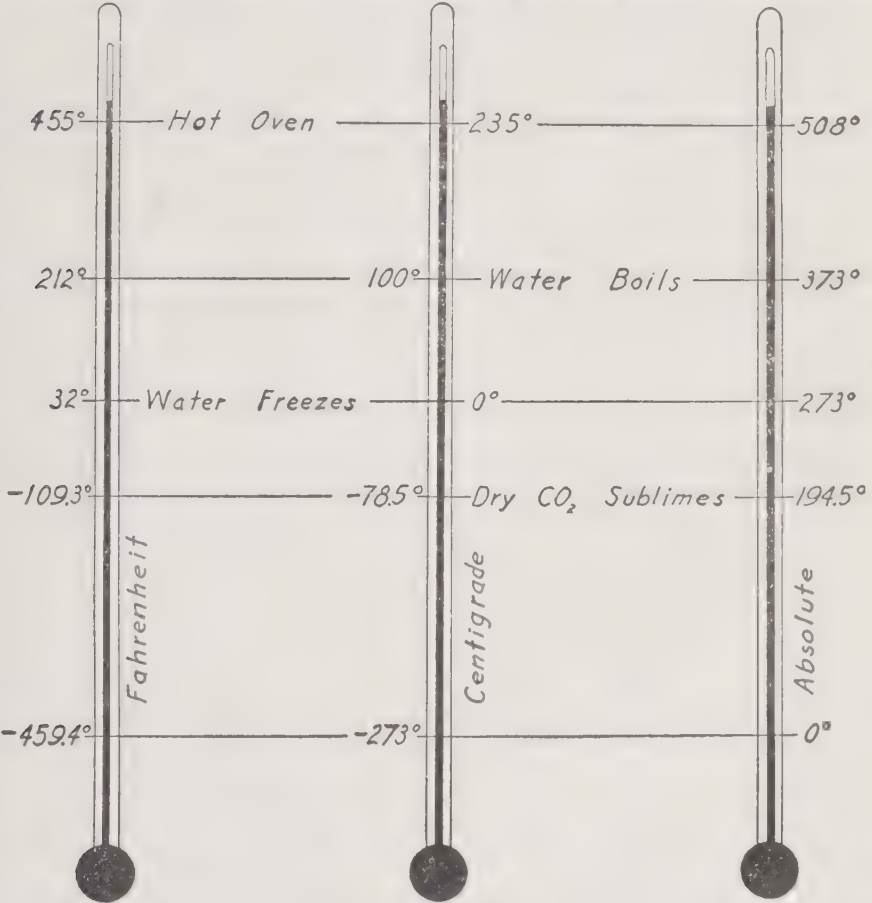


FIG. 14. Relationship between Centigrade, Absolute, and Fahrenheit Thermometer Scales

room temperature, the water will then occupy only 960 c.c. Perhaps you have had the experience of removing from the oven some light, puffy popovers, only to find that the hot gas in them, on cooling, diminished in volume and the pressure of the air around them caused them to collapse.

With solids and liquids the amount of expansion when heated is dependent upon the kind of matter. For a given temperature change, the expansion of aluminium is three times greater than the expansion of platinum. When mercury is heated, the increase in volume is more than twenty times greater than that of water. With gases, however, the change in volume is independent of the kind of gas. Whenever any gas at 0°C. is heated, it expands $1/273$ of the original volume for each degree heated. A gas contracts $1/273$ of the volume for each degree below 0°C. to which it is cooled. It is evident that if a gas could be cooled to -273°C. , the original volume should be decreased by $273/273$ of itself, or the volume should become zero. This might seem improbable, but every gas liquefies before it becomes cooled to -273°C. and in the liquid condition the gas laws no longer apply to its behavior.

It becomes a simple matter to calculate the volume-temperature change for gases if the temperature is read on an absolute thermometer scale constructed so that the divisions are all the same size as the centigrade divisions and so that $0^{\circ}\text{C.} = 273^{\circ}\text{A.}$ Other temperatures correspond as shown in the diagram (Fig. 14).

Charles' Law. — The statement of the volume-temperature law as expressed by Charles is as follows: *If the pressure remains constant, the volume of a given weight of gas is directly proportional to the absolute temperature.* The application of the law will be better understood if we consider some volume-temperature problems.

Problem 1: When 5 liters of gas at 18°C. (291°A.) are cooled to 0°C. (273°A.), what volume will the gas occupy?

Solution: Using the statement of Charles' Law in solving this problem, we may say that as the gas is cooled from 291°A. to 273°A. , its volume is decreased so that the gas will occupy a fractional part $\left(\frac{273}{291}\right)$ of the original volume. This is represented by the expression

$$5 \times \frac{273}{291} = 4.69 \text{ liters}$$

Problem 2: Fifteen hundred cubic centimeters of gas are collected at 20° C. (293° A.). What volume will the gas occupy at 100° C. (373° A.)?

Solution: In this case, the gas is heated from 293° A. to 373° A. and so its volume is increased. To obtain the new volume, the original volume may be multiplied by a fraction greater than unity, namely $\frac{373}{293}$. The change in volume of the gas is indicated by the following:

$$1,500 \times \frac{373}{293} = 1,909 \text{ c.c.}$$

When working volume-temperature problems it is necessary to consider the questions: Is the gas heated or cooled? What is the corresponding effect upon the volume? The next step is to multiply the original volume by a fraction which will satisfy the conditions of the problem. That is, the fraction will be less than unity if the volume is to be decreased, and greater than unity if the volume is to be increased.

Relationship of Volume to Pressure. — *Units of Pressure.*

The pressure of air in a tire or of steam in a pressure cooker is usually expressed in pounds per square inch. When the steam gauge of a pressure cooker stands at 15, the steam is exerting fifteen pounds pressure more than that of the atmosphere above it. It should be noted that the pressure exerted by the gas as it escapes through the pressure

gauge is equal to the pressure to which it would have to be subjected to prevent it from expanding in volume. In

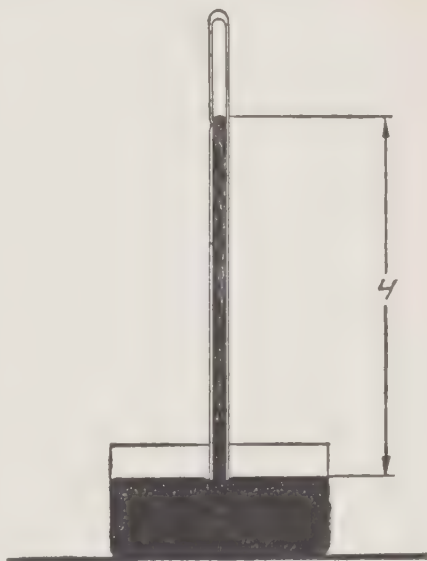


FIG. 15. Barometer

science, pressure is often expressed in grams per square centimeter; and on a barometer it is read in millimeters or inches of mercury.

A simple device which shows the principle of a barometer is illustrated in Figure 15. A tube, over 760 mm. long, and filled with mercury is inverted and supported in a dish of mercury. The pressure of the air on the surface of the mercury in the vessel holds the mercury in the tube to such a height (H) that it balances the pressure of the atmosphere on the mercury surface. Instead of calculating the weight of mercury, pressure is usually read directly as the height of the column of mercury in the tube. At sea-level the average height is 760 mm., and this is often called "one atmosphere of pressure."

Boyle's Law. The volume-pressure relationship of gases was expressed by Robert Boyle as follows: *If the temperature remains constant, the volume occupied by a given weight of gas is inversely proportional to the pressure.* The relationship "increase of pressure, decrease of volume" is easy to understand when we consider that the use of double pressure upon a volume of gas will decrease it to one half of the original volume. A few problems may make the application of the law clearer.

Problem 1: Ten liters of gas collected at 700 mm. pressure will occupy what volume at 760 mm.?

Solution: It is understood in this case that ten liters of gas may be in a container in which the pressure can be regulated by a movable piston. According to Boyle's Law, as the pressure is increased from 700 mm. to 760 mm., the volume of the gas is decreased so that it occupies a fractional part $\left(\frac{700}{760}\right)$ of the original volume. This is represented by the expression

$$10 \times \frac{700}{760} = 9.21 \text{ liters}$$

Problem 2: Twenty-five liters of gas at 900 mm. pressure are transferred to a container in which the gas is held at a pressure of 740 mm. What volume does the gas then occupy?

Solution: According to this problem, the pressure upon the gas

is decreased from 900 mm. to 740 mm. An increase in volume results from the decrease in pressure. To obtain the new volume occupied by the gas, the original volume may be multiplied by a fraction greater than unity, namely $\frac{900}{740}$. Thus the change in volume may be represented by the expression

$$25 \times \frac{900}{740} = 30.4 \text{ liters}$$

When working volume-pressure problems, it is necessary to consider the questions: Is the pressure increased or decreased? What is the corresponding effect upon the volume of gas? The next step is to multiply the original volume by a fraction which will satisfy the conditions of the problem. That is, the fraction will be less than unity if the volume is to be decreased, and greater than unity if the volume is to be increased.

Methods of Collecting Gases. — In Chapter III a method was described for collecting a measured quantity of gas. A cylinder is filled with liquid mercury and inverted over a vessel containing mercury (Fig. 5). When the exit tube of a generator bottle is placed under the cylinder containing mercury, the gas flows upward into the container as the mercury is displaced. Since liquid mercury does not evaporate at the temperature at which gases are usually collected, the gas obtained in this way contains no mercury vapor. The method is used when quantities of pure gas are needed for scientific work.

In a similar laboratory method, the cylinder is filled with water and inverted over a vessel containing water (Fig. 17). When the gas is collected by displacement of water, the conditions are somewhat different from those described in the preceding paragraph, because water has a tendency to evaporate, and thus the gas collected by displacement of water contains some water vapor mixed with the gas. Although the gas collected in this way is not as pure as that collected over mercury, the method is used for collecting gases for most laboratory procedures.

Vapor Pressure. — It may easily be demonstrated that the pressure of water vapor is dependent upon temperature. If a few cubic centimeters of water are introduced into the barometer tube (Fig. 16), part of the water immediately evaporates. The water vapor thus formed exerts its pressure on the surface of the

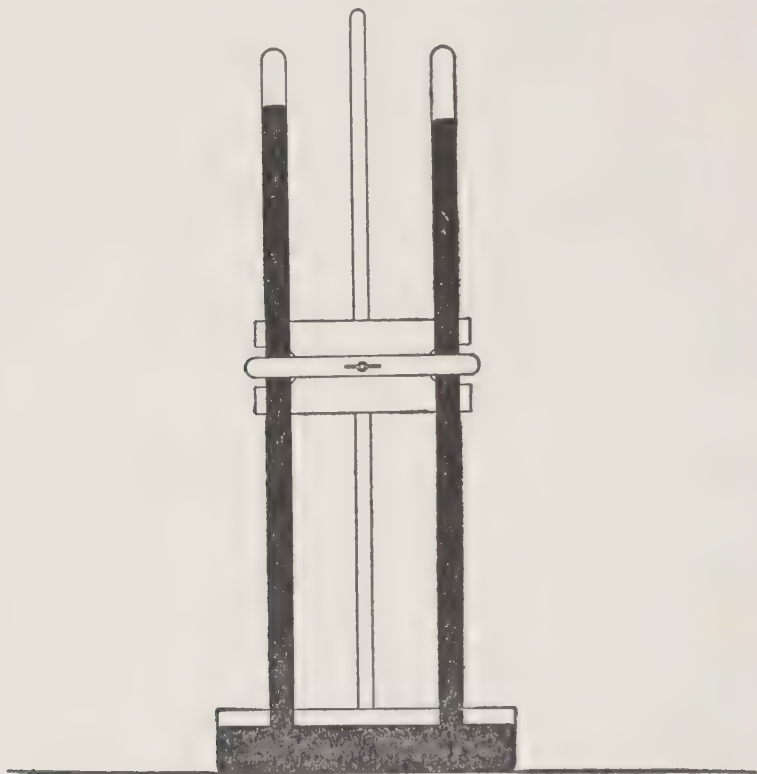


FIG. 16. Vapor Pressure

mercury. The pressure causes some of the mercury to be forced out of the tube. The water vapor pressure at the temperature of this experiment will then be the difference between the original height of the column of mercury and the height after water was introduced. The same experiment conducted at another temperature would give a different vapor pressure value.

The tendency of the water to evaporate is called **aqueous vapor tension**; the pressure exerted by the water vapor is called **aqueous**

vapor pressure. Under the conditions illustrated (at equilibrium) the vapor tension is equal to the vapor pressure, and both are dependent upon temperature. Section 3 in the Appendix gives the aqueous vapor pressure values (expressed in millimeters of mercury) for temperatures between 15° and 32° C.

Correction of a Gas Volume to Dry Gas. Partial Pressure. — When reading the volume of a gas collected over water, it is customary to have the water at the same level inside and outside of the measuring cylinder (Fig. 17). It is then that the total

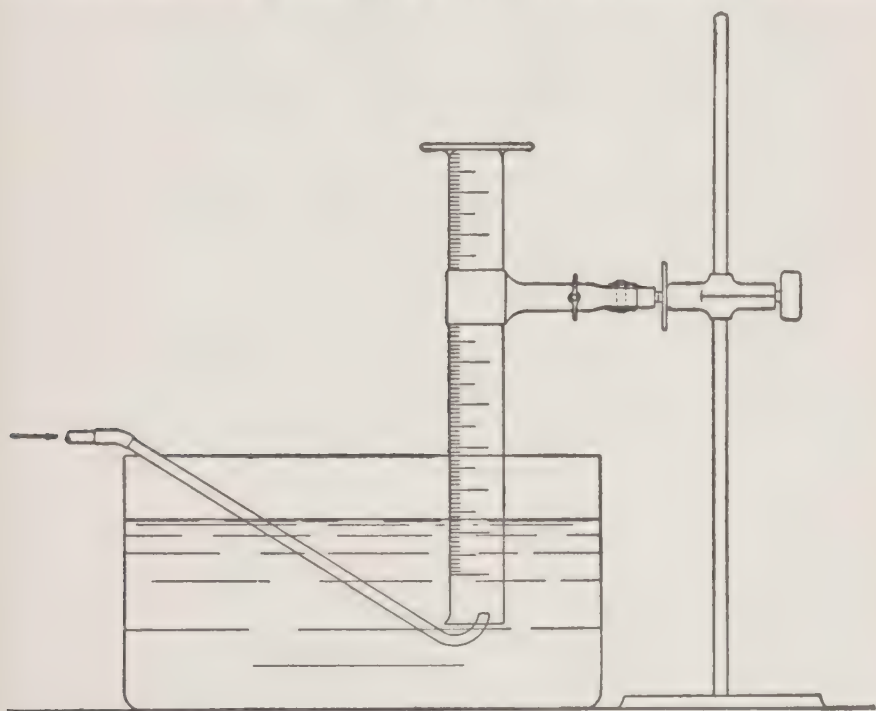


FIG. 17. Measuring a Volume of Gas Collected over Water

pressure of the mixture (gas plus water vapor) inside the cylinder is the same as the barometric pressure. The pressure exerted by each of the gases in the cylinder is known as its partial pressure. The total pressure of the mixture is the sum of the partial pressure of the dry gas and the partial pressure of the water vapor.

The vapor pressure of water at any temperature has been determined experimentally (Appendix, Section 3) and may be found by referring to this section. Hence the partial pressure due to dry gas is obtained by subtraction:

Barometric pressure — aqueous vapor pressure = pressure of dry gas (when all are expressed as mm. of mercury).

Using this vapor pressure correction, it is possible to obtain the volume of dry gas which corresponds to that of a gas plus water vapor mixture. The method is illustrated in the following problem: A volume of gas measures 2,000 c.c. as collected over water when the laboratory temperature is 20° C. (293° A.) and the barometer reads 740 mm. of pressure. What volume will the dry gas occupy at 0° C. (273° A.) and 760 mm. of pressure?

Solution: At 20° C. the aqueous vapor pressure is 17.5 mm. of mercury (Appendix). As indicated in the previous paragraph, the pressure of the gas is obtained by the expression

$$740 - 17.5 = 722.5 \text{ mm.}$$

The problem is set up according to the volume-temperature and volume-pressure laws, the first fraction representing the correction for temperature and the second fraction the correction for pressure:

$$2,000 \times \frac{273}{293} \times \frac{722.5}{760} = 1,771.5 \text{ c.c.}$$

Standard Temperature and Pressure. — Since the weight of gas in a given volume varies with temperature and pressure, chemists have decided that such determinations must be reduced to uniform conditions. They have therefore chosen 0° C. as standard temperature and 760 mm. (the average barometric pressure at sea level) as standard pressure. Whenever it is necessary to compare two or more gas volumes collected at different temperatures and pressures, the volume each would occupy at standard conditions is calculated. In the Appendix, a section is given showing the number of grams per liter of several gases

(Section 2). These values would have no meaning unless the volumes represented were measured at standard conditions.

A Further Application of the Gas Laws. — It may seem easier to understand these laws if they are expressed in terms of proportions. For example, the volume-temperature relationship (Charles' Law) may be written:

$$\frac{V_1}{V_x} = \frac{T_1}{T_2}$$

In this expression, V_1 is the original volume at the absolute temperature T_1 , and V_x is the changed volume at the absolute temperature T_2 . The volume-pressure relationship may be written:

$$\frac{V_x}{V_2} = \frac{P_2}{P_1}$$

In this expression, V_x is the intermediate volume (the answer to the volume-temperature expression) at the pressure P_1 , and V_2 is the final volume at the pressure P_2 .¹

One expression may be derived from these two ratios. Multiplying the two equations:

$$\frac{V_1}{V_x} \times \frac{V_x}{V_2} = \frac{T_1}{T_2} \times \frac{P_2}{P_1}$$

$$\text{Therefore: } \frac{V_1}{V_2} = \frac{T_1 P_2}{T_2 P_1}$$

$$\text{Or: } V_1 T_2 P_1 = V_2 T_1 P_2$$

¹ If, in working problems using the gas laws, it seems convenient to use the proportions as stated, a relationship between them may be more evident if each proportion is given in such a way that the original volume, and the original temperature or pressure, are placed at the left of the equation while the changed volume and temperature or pressure are placed at the right. The formulas would thus be expressed

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{and} \quad V_1 P_1 = V_2 P_2$$

Dividing each member of the equation by T_1T_2 and canceling terms,

$$\frac{V_1 \cancel{T_2} P_1}{T_1 \cancel{T_2}} = \frac{V_2 \cancel{T_1} P_2}{\cancel{T_1} T_2}, \quad \text{whence}$$

$$\frac{V_1 P_1}{T_1} = \frac{V_2 P_2}{T_2}$$

Thus the expression combining the two laws is the following:

$$\frac{V_1 P_1}{T_1} = \frac{V_2 P_2}{T_2}$$

Problem: A volume of gas measures five liters as collected over water at 18°C . (291°A .) and 720 mm. of pressure. What will be the volume of dry gas at standard temperature and pressure?

Solution: Using the combined formula,

$$\begin{array}{ll} V_1 = 5 \text{ liters} & V_2 = \text{the changed volume} \\ T_1 = 291^\circ \text{A.} & T_2 = 273^\circ \text{A.} \end{array}$$

Aqueous vapor tension = 15.4 mm.

$$P_1 = 720 - 15.4 = 704.6 \text{ mm.}$$

The equation becomes:

$$\begin{aligned} \frac{(5)}{(291)} \frac{(704.6)}{(291)} &= \frac{(V_2)}{(273)} \frac{(760)}{(273)} \\ V_2 &= \frac{(5)}{(760)} \frac{(704.6)}{(291)} \frac{(273)}{(273)} \\ V_2 &= 4.34 \text{ liters} \end{aligned}$$

THE MOLECULAR THEORY

Scientists have learned much concerning the molecular structure of matter that helps in the understanding of its physical characteristics. Although this knowledge is still designated as theory, most of it has been proven to be fact by a variety of experiments. The important points of the theory may be listed as follows:

1. **Size.** — The infinitesimal size of molecules has been discussed in Chapter II.

2. Molecular Attraction. — In gases, the molecules have slight attraction for each other. For this reason they distribute themselves far from each other in any given space, and will fill any containing vessel. This explains how odors may penetrate throughout a large building. Compared to the size of the container, the volume actually occupied by the molecules is extremely small. In other words, the volume in which a gas is dispersed is mostly space. Under compression the molecules are nearer together, since the space between them is reduced. It is because this space exists that molecules of gases respond to changes in pressure in a greater measure than liquids or solids. In liquids the molecules have enough attraction for each other to stay together and maintain a constant volume, but they may be pulled apart by gravity and thus take the shape of the container. In solids the molecules have a much greater attraction for each other and are not pulled apart easily. This explains the fact that solids have both a definite shape and a definite volume.

3. Motion of Particles. — The molecules of a gas move about rapidly in any given space, traveling at great speed in a straight line in every direction. Hydrogen molecules move more rapidly than those of other gases; the average velocity (20° C.) has been calculated to be 6,000 feet per second. Although the mass of each individual hydrogen molecule is extremely small, the combined effect of millions of them moving at this high average velocity and striking the sides of a containing vessel may result in a decided pressure. The pressure of the molecules of gas is evident when a great quantity of air is forced into an automobile tire. The smaller the volume occupied by a given weight of gas, the more pressure it exerts, and the greater the pressure that is needed to confine it in this space. Molecules of liquids and solids have less freedom of motion.

4. The Effect of Heat on the Motion of Particles. — The velocity with which molecules move increases when they are heated. As a solid is heated and the molecules move faster, they require more space, causing the entire solid to expand. This ex-

pansion of solids may be noted when the cracks of an iron stove become filled as the stove is heated. If the solid is heated sufficiently, the molecules will continue to increase in velocity until they move far enough apart to lose some of their intermolecular attraction and become a liquid.

In a similar way, the molecules of the liquid when heated will increase in velocity and require a greater volume. The expansion of a heated liquid is noted when a kettle filled with cold water overflows as it is heated. The rise and fall of mercury in thermometers is caused by the change in the velocity of the molecules and hence in their volume with a change in temperature.

When a liquid is heated sufficiently, the molecules move with such rapidity that they lose all attraction for each other and become a gas.

When a gas is heated, the increase in velocity of the molecules will cause a greater number of impacts and hence a greater pressure on the side of the containing vessel. It follows that the pressure exerted by a gas increases with temperature or, to state the same fact in another way, when the pressure is held constant the volume of a given weight of gas must increase as the temperature increases (Charles' Law). It is this increase in the velocity of molecules that causes the air pressure in an automobile tire to become higher on a hot summer day.

CHANGES IN PHYSICAL STATE

Solid and Liquid. — When ice melts in the hand causing a feeling of intense coldness, one has direct evidence that heat is absorbed in the physical change of a solid to a liquid. According to the molecular theory this heat is absorbed by the molecules of the solid as they increase in velocity and lose their intermolecular attraction to become a liquid. When water is frozen into a solid a similar quantity of heat is evolved or liberated as the freedom of motion of the molecules decreases. A mixture of ice and water at 760 mm. pressure will remain at 0° C. until the entire mass is warmed sufficiently to change it to a liquid, or cooled sufficiently to change it to a solid. It follows that the temperature (0° C.) at

which ice and water are in equilibrium at 760 mm. pressure is the melting point of ice and the freezing point of water.

The number of calories of heat absorbed when one gram of any crystalline solid changes to a liquid is called its **heat of fusion**. The number of calories of heat that are evolved when one gram of any liquid changes to a crystalline solid is equal to the heat of fusion and is called the **heat of solidification**. The heat of fusion of ice and heat of solidification of water is 80 calories.

Practical use is made of this absorption of heat in iced beverages because the melting ice absorbs heat from the beverage without changing temperature. Hot fudge may be cooled in a pan of ice and water; the melting ice absorbs heat from the candy mixture. When ice cream is frozen in a freezer, the ice and salt solution outside the can absorbs the heat that is liberated by the freezing cream.

Only crystalline solids have definite melting and freezing points and heat of fusion. In other solids, such as glass and sealing wax, which have no definite crystalline form, the atoms and molecules have no definite arrangement. These are said to be **amorphous** or **plastic solids**. They are sometimes considered to be very thick (viscous) liquids since, when they are heated and their molecules move more rapidly, they gradually become softer and more plastic and finally change to a true liquid.

Liquid and Gas. — Just as heat is absorbed when a solid changes to a liquid, more heat must be absorbed to increase the velocity of the molecules enough to give them the freedom of movement of a gas. In every liquid, even at low temperatures, some of the molecules will be moving rapidly enough to escape as a gas or vapor.² In this way water evaporates from wet clothes and from shallow pools. The tendency of a liquid to vaporize depends on the nature of the liquid and on its temperature. The tendency of the liquid to form vapor is called its **vapor tension**. Ether, alcohol, and perfumes have a high vapor tension at room temperatures.

As any liquid is heated, the increase in the velocity of the

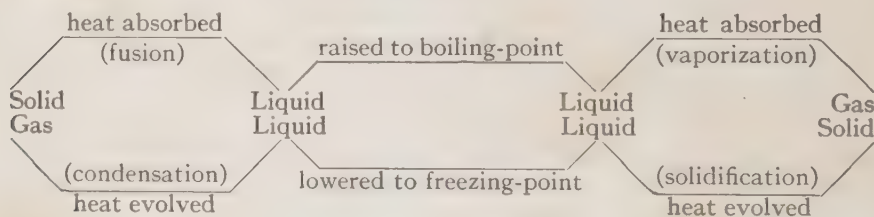
² Any gas which may be condensed to a liquid by increasing the pressure upon it without changing the temperature is designated a vapor.

molecules allows more of them to escape as a vapor, and the vapor tension is increased. At a certain temperature, characteristic for each liquid, this vapor tension, and thus the pressure exerted by the vapor, is equal to the pressure of 760 mm. of mercury (standard atmospheric pressure). This is called the **boiling-point**; as the vapor tension just exceeds the atmospheric pressure on the surface of the liquid, all the heat energy applied is absorbed by the changing of the liquid to a gas, causing the temperature of the liquid to remain constant.

The number of calories absorbed when one gram of liquid at its boiling-point changes to a gas is called the **heat of vaporization**. This same quantity of heat liberated when a gram of gas at the boiling-point changes to a liquid is called **heat of condensation**. The heat of vaporization and condensation for water is 540 calories.

It is this heat of condensation, liberated as steam changes to water at the boiling temperature, that makes a burn from steam more painful than a burn from hot water. Alcohol baths are cooling because as the alcohol evaporates from the body the heat of vaporization is absorbed.

The energy changes involved in changes in physical state are summarized in the following diagram:



It is of interest for a student to realize that the two temperatures mentioned in the preceding paragraphs, namely 100°C. as the boiling-point of water and 0°C. as the freezing-point of water, are the standard temperatures on which the centigrade thermometer is constructed. They are values so constant and reproducible as to be considered **calibration points**, which means that if any thermometer should register a temperature other than these mentioned (after a standard correction has been applied to account



Courtesy of Armour and Company, Chicago, Ill.

COOLING ROOM

A wholesale market beef cooler takes care of 1500 cattle until the meat is ready for shipment to consumers. The temperature is maintained constantly at 34° to 36° Fahrenheit.

for difference in pressure) for the boiling-point or freezing-point of water, the thermometer is inaccurate. The freezing-point (also melting-point) and boiling-point of other substances are sometimes used to check other temperatures on a thermometer scale.

Pressure Cooker. In the discussion of boiling-point it was noted that boiling temperature is dependent upon pressure. At standard pressure the boiling-point of pure water is 100°C . On Pike's Peak, where the atmospheric pressure is lower, the boiling temperature of water is so much lower that many kinds of food require longer cooking than in a locality where the pressure is higher. In direct contrast to this, we may consider a pressure cooker in which steam is enclosed and made to exert extra pressure within the

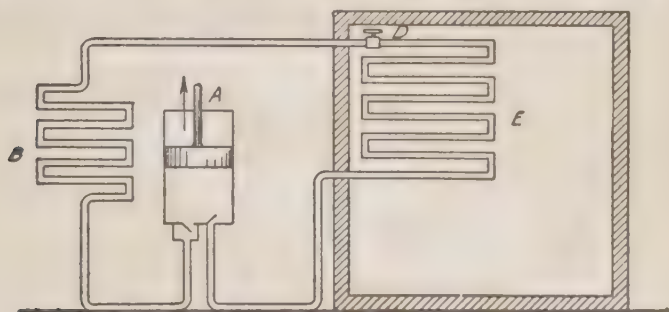


FIG. 18. The Mechanism of the Electric Refrigerator

vessel. This raises the boiling-point, since a higher temperature is required to cause the pressure of vapor from the contents of the vessel to exceed the pressure of steam upon them. At this higher temperature, vegetables will soften more quickly and bacteria are more easily destroyed. Most pressure cookers are designed to give nearly twenty pounds of steam pressure, which raises the boiling-point to about 125°C .

Mechanical Refrigeration. An interesting device has been perfected which provides the cooling units for the household electric refrigerators, for refrigerating rooms, and for the manufacture of ice. These cooling units operate through the use of a liquid which evaporates near the temperature of the freezing-point of water and has a high heat of vaporization. Liquid ammonia, methyl

chloride, sulphur dioxide, and "freon" (CF_2Cl_2) are examples of such substances. The principles involved in the process of refrigeration may be seen in Figure 18. The ammonia gas (or any one of the other gases) is led from the pipes *E* within the refrigerator to the compressor and is compressed by means of the piston *A*. The compressor usually operates by electricity. The compressing of the gas and the cooling in the coils *B* causes liquefaction. Through the expansion valve *D*, drops of the liquid are allowed to enter the coils within the refrigerator. Immediately the liquid evaporates to a gas and in doing so removes heat from the space surrounding the coils. The liquid, in changing to a gas, has done its work. The gas from the coils *E* is led back to the compressor to be used again in the same process. Refrigerating units are equipped with devices for regulating the rate of evaporation of the liquid in the coils *E*, and hence the temperature of the refrigerator.

Distillation. The separation of a pure liquid from other substances which are dissolved in it may be accomplished by distilla-

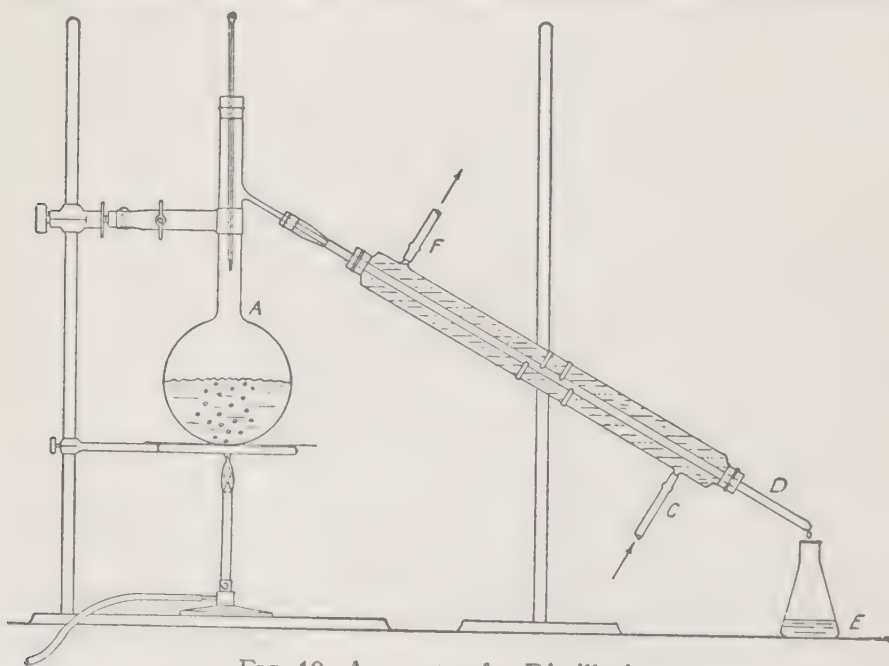


FIG. 19. Apparatus for Distillation

tion. The process consists in boiling the liquid to change it to a vapor and then condensing the vapor. An apparatus similar to the one illustrated in Figure 19 is usually used in the laboratory. The liquid is heated in the flask *A* and the vapor passes through the tube *D* of the condenser. Tube *D* is surrounded by cold water which enters at *C* and leaves the condenser at *F*. The vapor cools and condenses to a liquid which may be collected in the vessel *E*. There remains in flask *A* any substance which is not a gas at the temperature at which the liquid is boiling. The process may be used in the laboratory for the purification of water, for the separation of any liquid from dissolved or suspended matter, or for the separation of two liquids of widely different boiling-points.

QUESTIONS AND PROBLEMS

1. Explain why the expression "one liter of water" is more definite than "one liter of carbon dioxide."
2. Calculate the following temperatures: the freezing point of water, on the absolute scale; 0° A. on the centigrade scale; 200° C. on the absolute scale; 200° A. on the centigrade scale; 80° F. on the centigrade scale; 20° F. on the centigrade scale.
3. Locate each of the following points on both centigrade and absolute scales: 0° C., 105° C., -50° C., 100° A., -273° C., 293° A., 15° C.
4. Diagram a barometer and explain how it is used.
5. Explain three units in which the pressure of a gas may be expressed.
6. State the volume-temperature law. Explain the law in terms of the molecular theory.
7. State the volume-pressure law. Explain the law in terms of the molecular theory.
8. What is standard pressure? Express standard pressure in mm., in cm., and in inches of mercury. How does the average pressure of a laboratory compare with standard pressure?
9. What is standard temperature? Express standard temperature in degrees C., and in degrees A. How does the average temperature of a laboratory compare with standard temperature?
10. What is the effect of an increase in atmospheric pressure on the volume of gas collected in the laboratory? How does the volume of gas at atmospheric pressure compare with the volume at standard pressure?
11. What is the effect of an increase in temperature on the volume of a gas collected over water? How does the volume of gas at laboratory temperature compare with the volume at standard temperature?

12. Define vapor pressure. How does it affect the apparent volume of a gas that is collected by bubbling through water (as oxygen is collected in the laboratory)? Explain why a pure gas is obtained by collecting over mercury.
13. Upon what factor does the aqueous vapor pressure (or aqueous vapor tension) depend?
14. A volume of gas measures 400 c.c. as collected at 18°C . What will be the volume which this gas occupies at 25°C .?
15. A volume of dry gas measures eight liters when collected at a barometric pressure of 730 mm. What will be the volume of this gas at 760 mm. pressure?
16. Ten liters of dry hydrogen gas at 700 mm. pressure are subjected to a pressure of 780 mm. How many liters of gas are obtained? Explain why the answer differs from the original volume of gas.
17. Five hundred c.c. of dry hydrogen gas at 0°C . will occupy how many c.c. at 27°C .? Explain why the answer differs from the original volume of gas.
18. A cream puff contains 350 c.c. of gas in an oven at 220°C . What will be the volume of the gas at 20°C .?
19. A quantity of dry gas measures 500 c.c. at 20°C . and 780 mm. pressure. What volume will the gas occupy at standard temperature and pressure?
20. A volume of hydrogen gas measures five liters as collected over water in the laboratory at 25°C . and 720 mm. pressure. What volume will this amount of dry gas occupy at standard temperature and pressure? What will be the weight of hydrogen? (One liter of hydrogen gas at standard temperature and pressure weighs 0.0898 g.)
21. A cylinder of dry oxygen gas holds 4,000 c.c. when the gas is collected at 27°C . and 740 mm. pressure. What weight of oxygen is present? (One liter of oxygen gas at standard temperature and pressure weighs 1.429 g.)
22. A ten-liter vessel is filled with oxygen gas collected over water in a laboratory at 23°C . and at a barometric pressure of 742 mm. This amount of oxygen weighs 12.432 g. Calculate the weight of one liter of oxygen at standard temperature and pressure.
23. A quantity of hydrogen gas measures 2,200 c.c. as collected over water in a laboratory at 18°C . and 722 mm. pressure. The hydrogen gas collected weighs 0.1725 g. What is the weight of one liter of hydrogen gas as collected in the laboratory? What is the weight of one liter of hydrogen gas at standard temperature and pressure? Why are the weights not the same?
24. Five liters of oxygen gas are collected over water at 25°C . and 623 mm. pressure. How many c.c. of gas will be obtained when this volume is subjected to standard temperature and pressure? The total volume

- of gas weighs 5.158 g. What is the weight of 450 c.c. of oxygen at standard temperature and pressure?
25. A small cylinder holds 3.5 liters of dry air at 20° C. and 800 mm. pressure. What pressure would be exerted if the cylinder is placed in the sunshine and the gas assumes a temperature of 65° C., with no expansion of the cylinder?
 26. A cylinder has a capacity of 30 liters. It is filled with hydrogen at a pressure of 76,000 mm. when the temperature is 30° C. How many one-liter balloons will the hydrogen fill at 20° C. and 840 mm. pressure?
 27. Is heat liberated or absorbed in the following changes: (a) when ice cream is being frozen; (b) when air is compressed in a tire; (c) when sugar is melted; (d) when water evaporates; (e) when steam condenses to water; (f) when liquid air evaporates; (g) when alcohol evaporates?
 28. How does the molecular theory explain: (a) the increase in pressure of air in a tire when temperature increases; (b) diffusion of a gas throughout an open space (perfume from flowers); (c) evaporation of water at room temperature; (d) the rate of evaporation of alcohol and water?
 29. What name is applied to the following: (a) a solid with no definite shape or arrangement of atoms; (b) the heat evolved when a liquid changes to a solid; (c) the heat absorbed when a liquid changes to a gas; (d) the temperature at which the vapor tension of a liquid just exceeds the atmospheric pressure?
 30. Why does the hand feel cold when a few cubic centimeters of alcohol evaporate from it?
 31. Why is a burn from steam more painful than a burn from boiling water?
 32. Define *boiling-point*. What would be the effect of removing the air from a vessel that contains water on the boiling-point of the water? What is the effect of altitude on the boiling-point?
 33. Why do vegetables soften more quickly when cooked in a pressure cooker? Why do they soften more slowly when cooked in boiling water on a mountain top?
 34. Diagram and explain the action of the electric refrigerator described in the text.
 35. What is meant by distillation of water? Describe one apparatus used to distil water.
 36. Define *heat of fusion*, *heat of solidification*, *heat of vaporization*, *heat of condensation*. Why are these sometimes described as "latent heat"?
 37. Name four amorphous substances and four crystalline substances. How do they differ?

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CHAPTER IX

EXPERIMENTAL DETERMINATIONS OF MOLECULAR WEIGHT AND ATOMIC WEIGHT

A TABLE of atomic weights, as listed on the back cover of the book, represents much careful research. These weights are determined through measurements of gram-molecular weights, through analyses of many compounds containing the elements, and through experimental determinations of combining proportions of the elements. The methods here described are based on laboratory experiments which lead to the determination of gram-molecular weight, of approximate atomic weight, and finally to the exact atomic weight of elements.

Gram-Molecular Volume. — In Chapter V we learned that the gram-molecular weight of any substance represented 6.06×10^{23} molecules of it. For all gases, Avogadro's hypothesis states that this number of molecules will occupy the same volume if the pressure and temperature are constant. In other words, 32 grams of oxygen (O_2) or 2.016 grams of hydrogen (H_2) or 44 grams of carbon dioxide (CO_2) each represent 6.06×10^{23} molecules and occupy the same volume if collected at the same temperature and pressure. Laboratory experiments have shown that at standard conditions 22.4 liters is the volume that holds one gram-molecular weight of a gas. The calculation which determines this volume is simple if we use the experimental value for the weight of one liter of gas at standard conditions (Appendix, Section 2). The number of liters that holds the gram-molecular weight of oxygen is $32.00 \div 1.429 = 22.39$ liters; for hydrogen, the calculation is $2.016 \div 0.0898 = 22.45$ liters; and for chlorine $70.90 \div 3.16 = 22.43$ liters. This vessel of a standard size which closely approximates 22.4 liters then becomes a measuring unit, gram-molecular volume. At standard temperature and pressure, the weight of any gas contained in 22.4 liters is the gram-molecular

weight; the number of molecules of gas contained therein is 6.06×10^{23} . The following table may emphasize the significance of a formula in terms of gram-molecular weight, gram-molecular volume, and number of molecules:

TABLE VII

Gas	Formula	Gram-mol. wt.	Gram-mol. vol.	No. of molecules
Hydrogen	H ₂	2.016	22.4 l.	6.06×10^{23}
Oxygen	O ₂	32.000	22.4 l.	6.06×10^{23}
Nitrogen	N ₂	28.016	22.4 l.	6.06×10^{23}
Carbon dioxide	CO ₂	44.010	22.4 l.	6.06×10^{23}
Ammonia	NH ₃	17.032	22.4 l.	6.06×10^{23}

Laboratory Determination of Gram-Molecular Weight. — The gram-molecular volume furnishes a practical laboratory method for obtaining the gram-molecular weight of a gas. From experimental procedures, the weight of a given volume of gas at laboratory temperature and pressure may be obtained. The volume that the gas occupies at standard conditions may be calculated. Placing the volume of gas at standard conditions equal to the weight of gas, the weight of one liter of gas at standard conditions may be calculated. This weight multiplied by 22.4 gives the weight of gas which at standard conditions fills 22.4 liters, or the gram-molecular weight of the gas. A few problems will illustrate this principle.

Problem: One liter of chlorine gas at standard conditions weighs 3.16 g. Find the gram-molecular weight of the gas.

Solution: The weight of 22.4 liters of the gas is 22.4×3.16 or 70.784 g. This is the gram-molecular weight of the gas.

Problem: At standard temperature and pressure, 399 c.c. of dry oxygen gas weighs 0.572 g. From this fact calculate the gram-molecular weight of oxygen.

Solution: The weight of 22.4 liters of the gas may be determined by proportion. 399 c.c. (or 0.399 liter) weigh 0.572 g., 22.4 liters weigh x g.

$$\frac{0.399}{0.572} = \frac{22.4}{x}$$

$$x = 32 \text{ g.}$$

Therefore the gram-molecular weight of oxygen is 32.

Problem: A vessel contains 2.4 liters of dry carbon dioxide gas at 740 mm. pressure and 23° C. The gas weighs 4.24 g. Find the gram-molecular weight of carbon dioxide.

Solution: The volume of the gas at standard conditions may be determined as follows:

$$2.4 \times \frac{740}{760} \times \frac{273}{296} = 2.15 \text{ liters}$$

The weight of 2.15 liters of the gas is determined by the proportion:

$$\frac{2.15}{4.24} = \frac{22.4}{x}$$

$$x = 44.18 \text{ g.}$$

Therefore the gram-molecular weight of carbon dioxide, as obtained from these data, is 44.18 g.

This same method may be used to determine the weight of any volume of a gas.

Problem: The formula for ammonia is NH_3 . Find (1) its gram-molecular weight, (2) the weight of one liter of the gas, and (3) the weight of 350 c.c. of the gas.

Solution: (1) The gram-molecular weight of ammonia is the sum of the weights of the atoms, $14.008 + 3(1.008) = 17.032 \text{ g.}$

(2) Since 17.032 g. of ammonia fill 22.4 liters, one liter contains $17.032 \div 22.4$ or 0.76 g.

(3) When 22.4 liters contain 17.032 g., 350 c.c. (0.35 liter) contain how many grams?

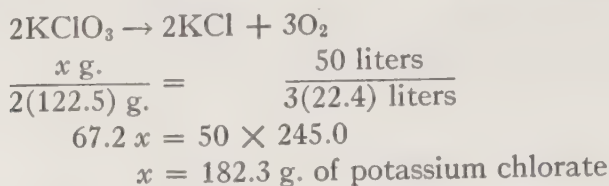
$$\frac{22.4}{17.032} = \frac{0.35}{x}$$

$$x = 0.26 \text{ g.}$$

Proportion Problems, using 22.4 liters. — A useful application of gram-molecular volume is illustrated in the following problems:

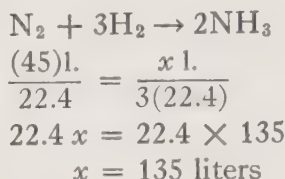
Problem: How many grams of potassium chlorate must be heated to obtain 50 liters of oxygen?

Solution: The equation for the reaction is as follows:



Problem: How many liters of hydrogen gas will combine directly with 45 liters of nitrogen gas to form ammonia?

Solution: The equation for the reaction is as follows:



A simpler calculation will show the relationship of liters in this problem. For convenience, we will repeat the proportion:

$$\frac{(45)\text{l.}}{22.4} = \frac{x \text{ l.}}{3(22.4)}$$

Since 22.4 liters occurs in the denominator of both parts of this proportion, it may be canceled, leaving the expression:

$$\frac{(45)\text{l.}}{1} = \frac{x \text{ l.}}{3}$$

$$x = 135 \text{ liters}$$

This is in accord with Avogadro's hypothesis. The liter volumes of gases at standard temperature and pressure contain the same number of molecules; therefore the gases unite by volume according to the ratio by molecules.

Determination of Approximate Atomic Weight. — A laboratory method for determining the approximate atomic weight of an element depends upon (1) determination of the gram-molecular weight of many compounds containing the element, (2) deter-

mination of the percentage of the element in each compound, and (3) a calculation to obtain the grams of the element present in the gram-molecular weight of each compound. Data used for the determination of the atomic weight of carbon are illustrated as follows:

<i>Compound</i>	<i>Wt. of 1 liter at standard conditions (experimental)</i>	<i>Gram-molecular wt. (calculate wt. of 22.4 liters)</i>	<i>Percentage of carbon in compound (ex- perimental)</i>	<i>Grams carbon in each gram- molecular wt. (percentage × g.-m. wt.)</i>
Carbon				
dioxide	1.964	43.99	27.3	12.01
Ethylene	1.250	28.00	85.4	23.91
Acetylene	1.162	26.03	92.3	24.02
Methane	0.715	16.01	75.0	12.00
Propane	1.965	44.00	8.18	35.99

If we study the data in the table, we find that, in the five carbon compounds mentioned, either twelve, twenty-four, or thirty-six grams of the gram-molecular weight is carbon. Since twelve grams is the smallest weight of carbon found in a gram-molecular weight of any gaseous compound studied, it is taken to represent an atomic weight of carbon. The larger numbers obtained represent two or three atoms of carbon in the molecules of gaseous ethylene, acetylene, and propane.

The atomic weight determined by this method is approximate, not exact. There are many chances for error in the determination of the weight of gas which fills 22.4 liters at standard temperature and pressure. The errors may be in the difficulties of experimental manipulation and deviations in the behavior of gases in response to temperature and pressure. It is necessary, however, to determine the approximate atomic weight of an element in order to interpret correctly the results of other experiments.

Determination of Combining Weight or Equivalent Weight. — Since most elements combine directly with oxygen, it is a simple process to determine accurately the weight of the element which

combines with a fixed weight of oxygen. It is convenient to use eight grams of oxygen as the reference weight, for this weight of oxygen unites with 1.008 grams of hydrogen. Therefore, as hydrogen is the lightest element, all combining weights will be greater than one. **Combining weight** or **equivalent weight** is the weight of an element which combines with or is equivalent to eight grams of oxygen.

An experiment used to determine the combining weight of magnesium serves to illustrate this principle. A weighed quantity of magnesium is burned in a porcelain crucible. As the magnesium combines with the oxygen of the air, magnesium oxide is formed as a white ash. After cooling, the crucible and magnesium oxide are weighed. To make sure that all the magnesium has united with oxygen, the crucible and contents are again heated, (a few drops of water may be added to change any magnesium nitride to the oxide), cooled, and weighed. This process must be repeated until two consecutive weighings are alike, which indicates that no more magnesium oxide has been formed. The following experimental results serve to illustrate the method used in calculating the combining weight of magnesium:

Weight of crucible, cover, and magnesium	19.252 g.
Weight of crucible and cover	<u>18.731 g.</u>
Weight of magnesium521 g.
Weight of crucible, cover, and magnesium oxide	19.5950 g.
Weight of crucible, cover, and magnesium	<u>19.2523 g.</u>
Weight of oxygen combined3427 g.

From the results obtained, the weight of magnesium which combined with 8 grams of oxygen may be calculated as follows:

$$\frac{.521}{.3427} = \frac{x}{8} \qquad x = 12.16$$

Experiments similar to the one described will give the weights of other elements which combine with eight grams of oxygen. In the table following, the results of several determinations are given.

TABLE VIII

COMBINING OR EQUIVALENT WEIGHTS

Magnesium.....	12.16
Hydrogen.....	1.008
Chlorine.....	35.457
Copper.....	31.78
Calcium.....	20.04
Aluminium.....	9.00

Since these weights of various elements each combine with eight grams of oxygen, it is safe to predict that the elements would combine with each other in the same proportion. That is, 1.008 grams of hydrogen combine with 35.457 grams of chlorine to form hydrogen chloride, and 31.78 grams of copper combine with 35.457 grams of chlorine to form copper chloride.

Multiple Proportions. — Among the examples of combining weights, there are several instances in which elements combine with eight grams of oxygen in two or more different proportions; in other words, there are two combining weights for the element. The formation of cuprous oxide and cupric oxide is one of many examples.

Cuprous oxide.....8 g. of oxygen is combined with 63.57 g. of copper
 Cupric oxide.....8 g. of oxygen is combined with 31.78 g. of copper

It should be noted that the varying weights of copper (31.78 g. and 63.57 g.) are in the ratio of 1:2. From this and other similar relationships, the general statement may be derived that elements unite in the ratio of their combining weights or in multiples of these weights. The **law of multiple proportion** is stated: *When two elements form more than one compound, the varying weights of one element which combine with a fixed weight of the other element are to each other as small whole numbers.*

Exact Atomic Weight. — As previously stated, combining weights may be determined with great precision. Nearly all elements combine directly with oxygen, and experiments similar to the one described in the foregoing paragraphs are easily carried out. The following table shows the relationship of combining weight to atomic weight.

TABLE IX

	<i>Combining Weight</i>	<i>Atomic Weight</i>
Oxygen	8.000 ($\times 2$)	16.00
Copper	31.785 ($\times 2$)	63.57
Chlorine	35.45 ($\times 1$)	35.45
Magnesium	12.16 ($\times 2$)	24.32
Hydrogen	1.008 ($\times 1$)	1.008
Aluminium	8.99 ($\times 3$)	26.97

The multiple which is used to convert the combining weight into the atomic weight is indicated in the table. Note that this multiple is the same as the valence of the element (Chapter VII). Experimental evidence of valence derived from the weight relation of elements entering into chemical change was known long before the present theories of atomic structure explained the basis for valence. Moreover, it was only from a study of combining weight and atomic weight data obtained from the accurate and painstaking experiments of scientists that the present theories of atomic structure could be evolved. Many scientists of today are at work in laboratories determining the combining weights of certain elements with the use of the most sensitive instruments and equipment in order to check and correct the atomic weights now in use. Each year an international committee of scientists reviews the work and usually some slight changes are recommended for the atomic weights of several elements.

QUESTIONS AND PROBLEMS

1. Distinguish between the terms: gram-atomic weight and gram-molecular weight. What is the gram-atomic weight and the gram-molecular weight of oxygen, of carbon, of iron, of chlorine?
2. From the formula, determine the weight of each of the following volumes of gas (at standard conditions):
 - (a) 22.4 liters of ammonia gas
 - (b) 67.2 liters of oxygen gas
 - (c) 22.4 liters of a gas with the formula COCl_2
 - (d) 1 liter of chlorine gas
 - (e) 1 liter of sulphur dioxide gas
 - (f) 3 liters of hydrogen gas
 - (g) 400 c.c. of carbon dioxide gas.

3. What is the significance of 22.4 liters? How many molecules are present in 22.4 liters of oxygen; in 44.8 liters of ammonia; in 22.4 liters of hydrogen?
4. If 4 liters of gas at standard conditions weigh 7.88 g., what is the gram-molecular weight of the gas?
5. At standard conditions, 8 liters of ammonia gas weigh 6.089 g. Use the data to calculate the gram-molecular weight. Determine the gram-molecular weight of ammonia from the formula for the gas.
6. At standard conditions, 700 c.c. of chlorine gas weigh 2.22 grams. Use the data to calculate the gram-molecular weight. Determine the gram-molecular weight of chlorine from the formula for the gas.
7. A gas used in electric refrigerators has the formula CF_2Cl_2 . Determine the gram-molecular weight and the weight of one liter of the gas. Calculate the percentage composition.
8. Calculate the percent of oxygen in each of the following compounds: (a) potassium chlorate, KClO_3 ; (b) sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$; (c) sand, SiO_2 .
9. From the data given, determine the gram-molecular weight of each of the following gases, measured at standard conditions:
 - (a) 500 c.c. of a gas weigh 0.714 g.
 - (b) 4 liters of a gas weigh 12.68 g.
 - (c) 1,500 c.c. of a gas weigh 2.94 g.
10. A vessel holds 300 c.c. of dry gas at 20°C . and 740 mm. pressure. What volume will the gas occupy at standard temperature and pressure? This volume of gas weighs 0.534 g. What is the gram-molecular weight of the gas?
11. Determine the volume at standard conditions which holds 2 grams of phosgene gas, formula COCl_2 .
12. A gas has the formula NO_2Cl . Find the weight of 450 c.c. of the gas.
13. In an experiment, a sample of 1.74 grams of silver oxide was heated until all the oxygen it contained had separated. The silver that remained weighed 1.62 grams. From these results calculate the combining weight of silver.
14. From the following data find the approximate atomic weight of chlorine.

<i>Compound</i>	<i>Weight of 1 liter</i>	<i>Gram- molecular weight</i>	<i>% of chlorine in a molecule</i>	<i>Percentage \times g.-mol. wt.</i>
Phosgene	4.42 g.		71.7	
Chloroform	5.33 g.		89.1	
Methyl chloride	2.25 g.		70.3	
Carbonyl chloride	6.87 g.		92.2	
Phosphorus chloride	6.14 g.		77.5	
Hydrogen chloride	1.63 g.		97.3	

15. Determine the approximate atomic weight of nitrogen by completing the following table:

<i>Gas</i>	<i>Weight per liter</i>	<i>Gram- molecular weight</i>	<i>Percentage of nitrogen</i>	<i>Percentage \times g.-mol. wt.</i>
Nitrogen	1.25		100.00	
Nitrous oxide	1.978		63.70	
Nitric oxide	1.340		46.74	
Ammonia	0.77		82.28	

16. Distinguish between the terms: combining or equivalent weight and atomic weight. When are they the same?
17. From the combining and atomic weights of the following elements, determine the valence of each element.

<i>Element</i>	<i>Combining weight</i>	<i>Atomic weight</i>	<i>Valence</i>
Carbon	3	12	
Sulphur	8	32	
Calcium	20	40	

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CHAPTER X

ACIDS, BASES, AND SALTS

Introduction. — On the kitchen shelf or other places in the home we may find, in disguised form, many of the compounds which are used in a chemistry laboratory. Among these are examples of acids, bases, and salts to be studied in this chapter. Lemon juice, vinegar, and sour milk contain acids which are familiar compounds in the laboratory. Lye and ammonia water are used for cleaning; milk of magnesia and lime-water are used to counteract acidity in the stomach. These compounds are known as bases in chemistry. Certain washing powders consist of sodium carbonate or sodium phosphate, while a laxative may be magnesium sulphate (Epsom salt) or sodium sulphate (Glauber's salt). Table salt is sodium chloride. As a class of substances, these are salts to the chemist. It is interesting to find such an array of chemical compounds in every home. In this chapter, we shall describe many of the characteristic properties and reactions of acids, bases, and salts.

Properties of Acids. — In Chapter VI, the suggestion was made that all acids contain hydrogen combined with other elements in such a way that the hydrogen is easily displaced by certain metals. By accepted custom, the chemist writes hydrogen first in the formula of an acid, as HCl and H_2SO_4 . Because of this similarity in composition, acids have many properties in common. For the present, we may consider an acid to be any compound, of formula similar to those mentioned, which shows the properties of an acid. A description of some of these characteristic properties follows:

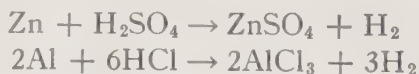
- (1) Acids have a sour taste. Think of the similarity in taste of vinegar, lemon juice, and tomatoes.
- (2) Acids react with baking soda. (The formula for baking soda

is NaHCO_3 .) The equation for the reaction of baking soda with an acid is as follows:

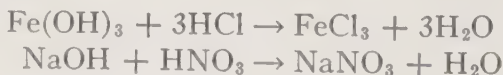


One product of the reaction is carbon dioxide gas, and it is this which causes the effervescence when baking soda reacts with any acid.

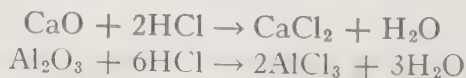
- (3) Acids weaken the fibers of textiles. Cotton fibers, especially, become tender when heated in an acid solution.
- (4) Acids change the color of many dyes. Most blue vegetable colors become red in acid solutions; for example, lemon juice or other fruit acids give grape juice a red color, and red cabbage juice, which is bluish red, becomes a clear bright red when vinegar is added. A pigment obtained from a lichen known as litmus, is used in the laboratory to detect acid because of its property of turning from blue to red in acid solution.
- (5) Acids react with all metals above hydrogen in the electrochemical series (Chapter IV). The hydrogen of the acid is displaced by the metals, and as a result hydrogen is evolved and a salt is formed which remains in solution. The following are examples of this reaction:



- (6) Acids react with the hydroxides of metals to form salts and water (see double decomposition reactions, Chapter VII); for example:

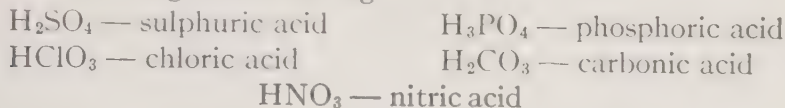


- (7) Acids react with oxides of metals to form a salt and water. The following equations illustrate the reaction:

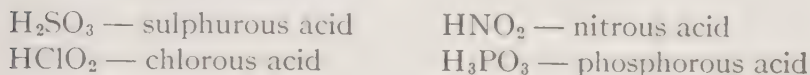


Formulas and Names of Acids. — The inorganic acids may conveniently be divided according to their names into three groups, as follows:

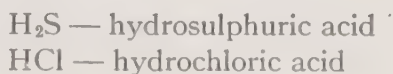
(1) Acids having names ending in *-ic*:



(2) Acids having names ending in *-ous*. (Note that each formula contains one less atom of oxygen than the corresponding formula in the preceding list.)



(3) *Binary acids*:



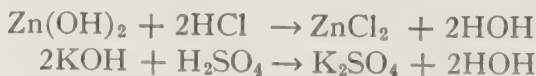
The acids which give the sour taste to fruits and vegetables are complex compounds containing carbon, hydrogen, and oxygen. As a class, they are often called **organic acids**. Two important acids of this kind are acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$ and oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$. In Chapter XXIX a more extended discussion of organic acids is given.

The formulas for acids consist of hydrogen and a negative element or radical. As we have learned in Chapter VII, the valence of the negative element or radical is determined by considering that, in every correct formula, the total positive charges are equal to the total negative charges. Therefore, the valence of the negative radical or element of an acid is equal to the total positive valence of the hydrogen. For example, in H_2^+S^- the valence of sulphur is minus two (derived from the fact that the total valence of hydrogen is plus two). In H_3PO_4 , the radical PO_4 has a valence of minus three; in $\text{HC}_2\text{H}_3\text{O}_2$, the radical $\text{C}_2\text{H}_3\text{O}_2$ has a valence of minus one. Formulas for acids must be learned; the formula

helps to associate the negative radical with its characteristic valence.

Properties of Bases. — A base may be defined as a compound in which a metal or the ammonium radical is combined with the hydroxide radical. In these formulas, the metal or ammonium radical (positive valence) is written first, followed by the hydroxide radical, as in NaOH and NH_4OH . Two of the most active bases — sodium hydroxide, NaOH, and potassium hydroxide, KOH — are known as **alkalies**. Because all bases have the hydroxide radical in combination with a metal, they have many properties in common. Among the characteristic properties are the following:

- (1) A basic solution has an alkaline taste. The solution is slippery or soapy to the touch.
- (2) Bases change red vegetable colors to blue. The dye litmus is used in the laboratory to distinguish between bases and acids. Litmus is red in acid solution, and changes to blue in basic solution. Red cabbage juice and grape juice become a decided blue in basic solution.
- (3) Bases disintegrate proteins. This property is especially evident when a basic solution is dropped on wool or silk textiles.
- (4) Bases react with fats to form soap. It is because of this reaction that lye (NaOH) and ammonia water (NH_4OH) are effective in cleaning greasy articles.
- (5) Bases react with acids to form salts and water. An example of this type of reaction has been given under the properties of acids. (See double decomposition reactions, Chapter VII.) Other examples are:



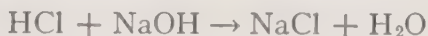
Formulas and Names of Bases. — According to the definition, formulas could be written for as many bases as there are metals (and including the ammonium radical). Actually, there are only a few compounds which are sufficiently soluble in water to exhibit

the properties of bases. The formulas and names for some of these are:

NH_4OH	ammonium hydroxide
NaOH	sodium hydroxide
KOH	potassium hydroxide

Calcium hydroxide, $\text{Ca}(\text{OH})_2$, and barium hydroxide, $\text{Ba}(\text{OH})_2$, are less soluble than the bases previously listed, but have the characteristic properties of bases. Magnesium hydroxide, $\text{Mg}(\text{OH})_2$, though not readily soluble, shows many characteristic reactions of a base. Similar statements may be made about zinc hydroxide, $\text{Zn}(\text{OH})_2$, aluminium hydroxide, $\text{Al}(\text{OH})_3$, and many other hydroxides.

Neutralization. — In listing the properties of acids and bases, it was shown that when their solutions are mixed a reaction takes place in which water and a salt are formed. (See double decomposition reactions, Chapter VII.) The reaction is known as neutralization, and is illustrated by the equation:



If the acid and base are in equivalent amounts (one gram-molecular weight of hydrogen chloride and one gram-molecular weight of sodium hydroxide), the resulting solution shows the properties of neither of the reactants.

Knowledge of neutralization may prove to be very helpful in the home. If a base is spilled on the hands or clothing (wash well with water first), the application of a mild acid may be used to stop the effect of the base. Vinegar and lemon juice are useful acids for this purpose. If an acid is spilled accidentally (wash well with water), its effect may be checked quickly by the addition of lime-water or ammonia water. Lime-water is an "antidote" for an acid taken into the stomach. Milk of magnesia (magnesium hydroxide) is a medicine used to neutralize acidity in the stomach. A lemon or vinegar rinse after a shampoo will neutralize any molecules of base left on the hair from the soap.

The following reaction of baking soda with acid was mentioned as a property of acids:



It is evident that there are no acids in the products of this reaction; that is, the hydrochloric acid has been "neutralized" by the baking soda. Since all carbonates react in a similar way with acids, carbonates may function as a base in counteracting acidity. A "pinch" of baking soda with tomato juice or fruit juices makes the juice taste less sour; baking soda (bicarbonate of soda) is a medicine, too, used to neutralize acidity in the stomach.

Properties of Salts. — In the foregoing paragraphs, it is pointed out that the term, salt, is applied to the product formed by the neutralization of a base with an acid. In other words, a **salt** is defined as a compound which is composed of a metal or the ammonium radical combined with the negative radical or element of an acid. Unlike acids or bases, salts have no element or radical common to all of them; consequently there are no properties characteristic of all salts. They are usually crystalline solids, but the taste, color, solubility in water, reaction toward litmus, and reaction toward metals varies with the kind of salt.

Formulas and Names of Salts. — Because each base can form a salt with each acid, a much greater variety of salts is possible than of acids or bases. The name of a salt is derived from the constituent metal (or ammonium radical), and the acid from which the salt is made. The salts formed from the binary acids, hydrochloric and hydrosulphuric, have names ending in **-ide** as in all binary compounds; for example, the zinc salt of hydrosulphuric acid, ZnS , is named zinc sulphide. All other acids having names ending in **-ic** form salts with names ending in **-ate**; for example, the calcium salt of nitric acid, $\text{Ca}(\text{NO}_3)_2$, is calcium nitrate and the calcium salt of acetic acid, $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$, is calcium acetate. Acids having names ending in **-ous** form salts with names ending in **-ite**; for example, the magnesium salt of phosphorous acid,

$\text{Mg}_3(\text{PO}_3)_3$, is magnesium phosphite. The relationship of the acids and the corresponding sodium salt is shown as follows:

H_2SO_4	sulphuric	Na_2SO_4	sodium sulphate
HClO_3	chloric	NaClO_3	sodium chlorate
HNO_3	nitric	NaNO_3	sodium nitrate
H_3PO_4	phosphoric	Na_3PO_4	sodium phosphate
H_2CO_3	carbonic	Na_2CO_3	sodium carbonate
$\text{HC}_2\text{H}_3\text{O}_2$	acetic	$\text{NaC}_2\text{H}_3\text{O}_2$	sodium acetate
$\text{H}_2\text{C}_2\text{O}_4$	oxalic	$\text{Na}_2\text{C}_2\text{O}_4$	sodium oxalate

H_2SO_3	sulphurous	Na_2SO_3	sodium sulphite
HClO_2	chlorous	NaClO_2	sodium chlorite
HNO_2	nitrous	NaNO_2	sodium nitrite
H_3PO_3	phosphorous	Na_3PO_3	sodium phosphite

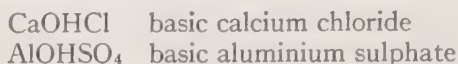
H_2S	hydrosulphuric	Na_2S	sodium sulphide
HCl	hydrochloric	NaCl	sodium chloride

[It is helpful to write equations showing the reaction of each acid with the base, sodium hydroxide, to form the salts. This may be followed by writing similar neutralization reactions using other bases such as barium hydroxide, ammonium hydroxide, or ferric hydroxide. See questions at the end of this chapter.]

Acid, Mixed, and Basic Salts. — When an acid radical has a valence of two or more, it is possible that it may be combined with different positive elements. In this way, such compounds as the following may be formed:

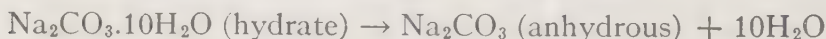
NaHSO_4	sodium hydrogen sulphate (or sodium bisulphate)
NH_4HSO_4	ammonium hydrogen sulphate (or ammonium bisulphate)
NaH_2PO_4	sodium dihydrogen phosphate
NaKCO_3	sodium potassium carbonate
$\text{NaAl}(\text{SO}_4)_2$	sodium aluminium sulphate

When hydrogen and a metal combine with an acid radical, the compound formed is an **acid salt**, such as NaHSO_4 . When two metals combine with an acid radical, the compound formed is a **mixed salt**, such as NaKCO_3 . Certain metals which have a valence of two or more may combine with hydroxide and an acid radical. In this way, the following **basic salts** may be formed:



In these compounds, the valence of the metal is satisfied by the hydroxyl group and the negative radical of an acid. Another type of mixed salt is one in which a metal is combined with two acid radicals. Bleaching-powder, $\text{Ca}(\text{ClO})\text{Cl}$, is a salt of this type.

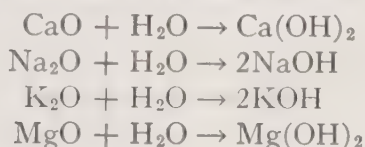
Hydrates. — Many salts have the property of forming a compound with a definite amount of water. The water is combined in a somewhat unstable way, since heat or desiccation easily removes it. These compounds are called **hydrates**. Copper sulphate, a colorless salt, is most familiar as a blue crystalline hydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Crystals of borax have the formula $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. Washing soda is usually obtained from the store as $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. Thus, when one buys crystals of washing soda, over half of the weight is water. When hydrates are heated, the water evaporates, and the dry powder remaining is said to be anhydrous. This is represented by the equation:



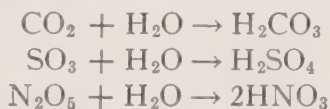
The addition of water to anhydrous substances or removal of water from hydrates may be a spontaneous process. For example, when the blue crystals of the hydrate copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, are exposed in a dry atmosphere, the water of hydration leaves the crystal and the gray anhydrous copper sulphate is formed. In an intermediate way, crystals containing less water may be formed as $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, and finally the anhydrous salt, CuSO_4 . This process of giving off water of hydration from a crystal is known as **efflorescence**. The hydrate is efflorescent. Many anhydrous crystals will take on water of hydration when exposed in a moist atmosphere. A dusty road

covered with powdered calcium chloride (anhydrous) soon appears moist because the anhydrous calcium chloride takes water from the air to form the hydrate $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. Enough water may be taken to make the hydrate appear to be dissolved in it. This process of taking up water of hydration by a salt is known as **deliquescence**. The anhydrous salt is deliquescent. An impurity sometimes present in table salt is a deliquescent compound, magnesium chloride. This causes much inconvenience when the salt appears to be too moist to pass through the salt-shaker.

Anhydrides of Acids and Bases. — Many oxides react with water to form a base or an acid. When an oxide of a metal reacts with water, a base is formed as shown by the reactions:



When an oxide of a non-metal reacts with water, an acid is formed as shown by the reactions:



Oxides of metals are called basic anhydrides, and oxides of non-metals are called acid anhydrides. All bases and all acids having oxygen in their formulas have anhydrides. Moreover, the valence of the principal element in the base or acid is the same as in the corresponding anhydride. A few examples will make this relationship clear. Al_2O_3 is the basic anhydride of Al(OH)_3 (the valence of aluminium is positive three in both compounds); N_2O_5 is the acid anhydride of HNO_3 (the valence of nitrogen ¹ is positive five in both compounds).

¹ To determine the valence of elements in compounds containing three kinds of atoms, it is necessary to use the familiar rule that in any correctly written formula, the total positive valence is equal to the total negative valence. In HNO_3 , the valence of hydrogen is positive one, and the total valence of the three oxygen atoms is negative six. The nitrogen, therefore, must have a valence of positive five to make the compound neutral.

The relationship of several bases and acids to the corresponding anhydride is shown in the following:

Mg(OH) ₂	MgO	H ₂ SO ₄	SO ₃
NaOH.....	Na ₂ O	H ₃ PO ₄	P ₂ O ₅
Ba(OH) ₂	BaO	HNO ₃	N ₂ O ₅

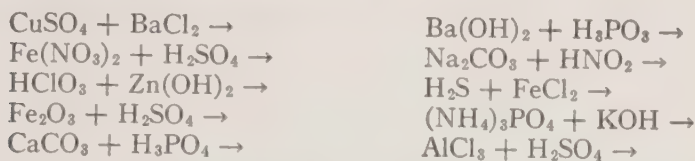
QUESTIONS AND PROBLEMS

1. Prepare a table showing the comparison of acids and bases with reference to composition, taste, effect on litmus, and effect on textiles.
2. Why do not all salts have similar properties, as do acids and bases?
3. Write the equations for the reaction of sulphuric acid on the metals zinc, magnesium, and aluminium. With the same metals, write equations using hydrochloric acid and phosphoric acid.
4. Write equations for the reaction of nitric acid on the following: zinc oxide, silver oxide, ferric oxide, copper oxide. Using the same oxides, write equations for the reaction with sulphuric acid and with hydrochloric acid.
5. Write equations for the reaction of phosphorous acid with the bases sodium hydroxide, calcium hydroxide, aluminium hydroxide, barium hydroxide, potassium hydroxide. Using the same bases, write equations with carbonic acid and with sulphurous acid. What is this type of reaction called?
6. Write formulas for the following compounds; classify as acids, bases, or salts:

zinc nitrate
zinc nitrite
potassium sulphate
potassium sulphite
potassium sulphide
silver chlorate
silver chlorite
calcium carbonate
sodium phosphate
sodium phosphite
barium hydroxide
mercury chloride
ammonium nitrate
ammonium nitrite
copper sulphate
magnesium nitrate
magnesium nitrite

silver sulphide
potassium nitrite
zinc chlorate
barium phosphate
copper sulphide
zinc phosphite
silver sulphate
ferric nitrate
ammonium sulphide
potassium chloride
mercury nitrate
mercury sulphate
calcium chlorate
sodium hydroxide
calcium hydroxide
aluminium sulphate
aluminium phosphate

7. Complete and balance the following equations:



Name the reacting substances and the products. Tell whether they are acids, bases, or salts.

8. Write balanced equations for the following; name the salt formed in the product:

- (1) calcium hydroxide with phosphoric acid
- (2) sodium hydroxide with sulphurous acid
- (3) magnesium hydroxide with chloric acid
- (4) zinc hydroxide with acetic acid
- (5) potassium hydroxide with phosphorous acid

9. Name the following compounds, and tell the type of salt (normal, acid, basic, mixed) that each represents:

- | | |
|----------------------------------|----------------------------------|
| (1) Na_2HPO_4 | (6) NaKCO_3 |
| (2) $\text{Mg}_3(\text{PO}_3)_2$ | (7) Al(OH)SO_3 |
| (3) NaKSO_4 | (8) CaHPO_3 |
| (4) $\text{Ca(ClO}_2)_2$ | (9) MgNH_4PO_4 |
| (5) Zn(OH)NO_3 | (10) $(\text{NH}_4)\text{HCO}_3$ |

10. Write formulas and names for five normal salts of calcium, each having names that end in -ate; four normal salts that have names ending in -ite; and two normal salts that have names ending in -ide.

11. Write formulas for five salts of acetic acid, and for five salts of oxalic acid.

12. What is a hydrate? How can it be shown in the laboratory that blue vitriol ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) is a hydrate?

13. Define neutralization. Compare the properties of the product with those of the original reactants. Write two neutralization reactions.

14. Would an acid or a base be more effective in removing each of the following stains from a glass surface: (a) a deposit of lime, CaO ; (b) grease; (c) milk of magnesia, Mg(OH)_2 ; (d) iron rust; (e) dried gelatin (protein); (f) baking soda?

15. Write equations to show the preparation of nitric acid from its anhydride, N_2O_5 ; of nitrous acid from its anhydride, N_2O_3 ; and of sulphuric acid from its anhydride, SO_3 . Indicate the valence of the principal element in the anhydride and in the acid.

16. Write equations to show the preparation of magnesium hydroxide from MgO ; of sodium hydroxide from Na_2O ; and of potassium hydroxide from K_2O . Indicate the valence of the metal in the base and in the basic anhydride.
17. How many grams of calcium phosphate will be formed when calcium hydroxide is neutralized by 15 grams of phosphoric acid?
18. How many grams of sodium hydroxide will be neutralized by 35 c.c. of phosphoric acid which contains .042 gram of phosphoric acid per c.c. of solution?
19. How many grams of potassium hydroxide are required to neutralize 40 grams of sulphuric acid?
20. How many liters of hydrogen sulphide gas would be formed by the reaction of hydrochloric acid with 30 grams of ferrous sulphide?
21. How many liters of hydrogen gas would be formed by the action of hydrochloric acid on 25 grams of aluminium?

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Lowe, Belle, *Experimental Cookery* (John Wiley and Sons, Inc., New York, 1937), Ch. IV.

CHAPTER XI

QUANTITATIVE REACTIONS OF ACIDS AND BASES

Indicators. — Litmus solution or litmus paper has been mentioned as a substance which has a red color in the presence of an acid and changes to a blue color in the presence of a base. Using litmus the progress of a neutralization reaction may be followed. That is, when a base is added to an acid colored with pink litmus, the color gradually changes to violet. When enough base has been added to neutralize all the acid, the next drop of base causes a distinct blue color to appear as the base predominates in the solution. **Indicators** are dyes which, like litmus, have different colors in acidic and in basic solutions. They are used in quantitative studies of acids and bases. Some useful indicators, with their characteristic colors, are:

<i>Indicator</i>	<i>Acid</i>	<i>Base</i>	<i>Neutral</i>
Litmus	pink	blue	violet
Phenolphthalein	colorless	red	pale pink
Methyl orange	red	yellow	orange
Brom thymol blue	yellow	blue	green
Congo red	blue	red	violet

Molar Solutions. — As was shown in Chapter III, the number of grams of solute in a given volume of solvent may be expressed in several different ways. For certain purposes, molar solutions are convenient. A **molar solution** contains one gram-molecular weight of solute in each liter of solution. The concentration of solutions having more or less than one molar weight per liter may be expressed as multiples or fractions of molar. The following calculations illustrate this principle:

(1) How many grams of nitric acid will be used in making one liter of a two-molar solution of the acid?

Calculation: The gram-molecular weight of nitric acid, HNO_3 , is:

$$1 + 14 + 48 = 63$$

Therefore, a molar solution contains 63 grams of nitric acid per liter, while a two-molar solution contains 126 grams of nitric acid per liter.

(2) How many grams of sodium sulphate are present in 150 c.c. of a one-fourth molar solution of the salt?

Calculation: The gram-molecular weight of sodium sulphate, Na_2SO_4 , is:

$$(2 \times 23) + 32 + (4 \times 16) = 142$$

Therefore, a molar solution contains 142 g. of sodium sulphate per liter. A one-fourth molar solution contains $142/4$, or 35.5 g. per liter. In 150 c.c. of the solution, there would be 0.150 of 35.5 grams, or 5.325 grams, of sodium sulphate.

(3) What is the molar concentration of a solution of sulphuric acid which contains 19.6 grams of acid per liter of solution?

Calculation: The gram-molecular weight of sulphuric acid, H_2SO_4 , is:

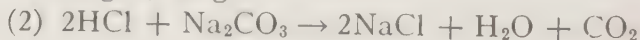
$$(2 \times 1) + 32 + (4 \times 16) = 98$$

Therefore, a molar solution contains 98 grams of sulphuric acid per liter. A solution that contains only 19.6 grams of acid per liter is $19.6/98$, or one-fifth molar.

Normal Solutions. — A study of the following equations will show that compounds react in the proportion indicated by a balanced equation, which is not always molecule for molecule.



$$36 \text{ g.} + 40 \text{ g.}$$



$$72 \text{ g.} + 106 \text{ g.}$$

In equation 1, the reacting proportion is that of the gram-molecular weights of hydrogen chloride (36 g.) and of sodium hydroxide (40 g.). Thus it is evident that one liter (or 1 c.c.) of a molar solution of hydrochloric acid would exactly react with one liter

(or 1 c.c.) of a molar solution of sodium hydroxide. In equation 2, the reacting proportion is that of two gram-molecular weights of hydrogen chloride (72 g.) and one gram-molecular weight of sodium carbonate (106 g.). Thus two liters of a molar solution of hydrochloric acid would exactly react with one liter of a molar solution of sodium carbonate. To put the second equation on the same basis as the first equation, we would have to say that one gram-molecular weight of hydrogen chloride (36 g.) will neutralize one half of a gram-molecular weight of sodium carbonate (53 g.). In these amounts, then, one liter (or 1 c.c.) of a molar solution of hydrochloric acid would exactly react with one liter (or 1 c.c.) of a half-molar solution of sodium carbonate. Since 36 g. of hydrogen chloride combines exactly with 40 g. of sodium hydroxide and with 53 g. of sodium carbonate, these weights are known as **gram-equivalent weights**. A **normal solution** contains a gram-equivalent weight of an acid, base, or salt per liter of solution. That is, a normal solution contains a weight of acid corresponding to 1.008 g. of hydrogen or a weight of base corresponding to 17.008 g. of hydroxyl ion, or a weight of salt corresponding to the equivalent of 1.008 g. of hydrogen. The gram-equivalent weight for metals is the atomic weight divided by the valence, as was shown in Chapter IX. Table X shows the relation between gram-molecular weight (for a molar solution) and gram-equiva-

TABLE X

<i>Compound</i>	<i>Formula</i>	<i>Gram-mol. weight</i>	<i>Gram-equiv. weight</i>	<i>Weight for 1 l. .1 N soln.</i>
Hydrochloric acid	HCl	36.465	36.465	3.6465
Sulphuric acid	H ₂ SO ₄	98.076	49.038	4.9038
Phosphoric acid	H ₃ PO ₄	98.004	32.668	3.2668
Sodium hydroxide	NaOH	40.005	40.005	4.0005
Sodium carbonate	Na ₂ CO ₃	106.004	53.002	5.3002
Calcium hydroxide *	Ca(OH) ₂	74.096	37.048	
Barium chloride (hydrate)	BaCl ₂ ·2H ₂ O	244.338	122.169	12.2169

* The solubility of calcium hydroxide is about 1.7 g. per liter. In other words, the most concentrated solution of calcium hydroxide that can be made is 0.046 N.

lent weight (for a normal solution) for several compounds (in terms of exact weights).

Application of Normal Solutions. — From Table X it is evident that a solution may be normal, tenth normal, or any multiple or fractional part of normal, depending on whether there is one gram-equivalent weight or a multiple or fractional part of the gram-equivalent weight per liter of solution. The multiple or fraction is termed the **normality** of the solution.

Normal solutions are devised in such a way that any volume of a solution of a given normality will react with or be equivalent to an equal volume of a solution of the same normality. For example, 50 c.c. of a 2 normal acid will neutralize 50 c.c. of a 2 normal solution of any base. Moreover, if 50 c.c. of a 2 normal solution of an acid will neutralize only 25 c.c. of a solution of a base, we know that the normality of the base must be double the normality of the acid or four normal. This principle is expressed in the general rule that in any experiment in which the volume of acid needed to neutralize or react with a certain volume of a base is determined, the c.c. of acid used multiplied by its normality is equal to the c.c. of base used multiplied by its normality, or:

$$\text{c.c. of acid} \times \text{normality} = \text{c.c. of base} \times \text{normality}.$$

Problem: How many grams of sulphuric acid are present in 30 c.c. of one-half normal (0.5 N) solution?

Solution:

Gram-molecular weight — $\text{H}_2\text{SO}_4 = 98 \text{ g.}$

Gram-equivalent weight is $\frac{98}{2} = 49 \text{ g.}$

A solution of sulphuric acid which is 0.5 N contains $49 \div 2$, or 24.5 g. per liter.

Thirty c.c. of solution is 0.030 liter. Therefore, thirty c.c. of solution contains $.030 \times 24.5 \text{ g.} = 0.735 \text{ g.}$ of sulphuric acid.

Problem: How many grams of oxalic acid will be required to prepare 20 liters of 0.3 N solution?

Solution:

Gram-molecular weight — $\text{H}_2\text{C}_2\text{O}_4 = 90 \text{ g.}$

Gram-equivalent weight is $\frac{90}{2} = 45 \text{ g.}$

A solution of oxalic acid that is 0.3 N contains $45 \times 0.3 = 13.5 \text{ g.}$ per liter. Twenty liters would contain $20 \times 13.5 = 270 \text{ g.}$ of oxalic acid.

Problem: Find the normality of a solution of phosphoric acid which contains 7.84 grams in 400 c.c.

Solution:

A solution that contains 7.84 g. in 400 c.c. contains 0.0196 g. per c.c., or 19.6 g. per liter.

Gram-molecular weight — $\text{H}_3\text{PO}_4 = 98 \text{ g.}$

Gram-equivalent weight is $\frac{98}{3} = 32.68 \text{ g.}$

A normal solution of phosphoric acid contains 32.68 g. per liter. The solution mentioned then is $19.6/32.68 = 0.6 \text{ N.}$

Problem: If 40 c.c. of a one-fourth normal solution of hydrochloric acid is exactly neutralized by 30 c.c. of a sodium hydroxide solution, find the normality of the sodium hydroxide.

Solution:

c.c. of acid \times normality = c.c. of base \times normality

$$40 \times 0.25 = 30 x$$

$$x = \frac{40 \times 0.25}{30}$$

$$x = 0.33 \text{ N.}$$

Titration. — The process of titration is used to determine quantitatively the concentration of acid, base, or salt in a solution. The process is of inestimable value in advanced chemistry work and in industrial and research laboratories. When the manager of a pickle factory wishes to know the concentration of the vinegar being used, he can determine it quickly by titration. In hospitals, the acidity of the contents of a patient's stomach may be determined by titration of a sample taken under controlled conditions. In experimental cookery and in nutrition problems,

the acidity of foods may be an important factor and may be determined by titration. A titration experiment is carried out in the following manner:

Some of the acid solution to be tested is poured into a burette (A, Fig. 20) which is a glass tube graduated to measure parts of a cubic centimeter and fitted with a stop-cock at the bottom from which the liquid may be drawn a drop at a time. Liquids may be measured accurately by this method. The burette, B, is filled with a basic solution of known concentration. This may be a solution of sodium hydroxide. The reading of both burettes in cubic centimeters should be taken at the beginning of the experiment. Then a definite volume of acid is drawn from the burette A into a clean beaker. A few drops of indicator are added, and the sodium hydroxide solution from B is titrated a drop at a time into the mixture in the beaker until the indicator shows the mixture to be neutral. In order to ensure accuracy, the titration is repeated three or four times and the results averaged. From these results, the concentration of the acid solution may be calculated. A specific example will make clear the calculation.

A sodium hydroxide solution was used which contained 5 g. of sodium hydroxide in 100 c.c. of solution. When vinegar was titrated against this solution, the average of three titrations showed that 20 c.c. of vinegar were neutralized by 13.8 c.c. of sodium hydroxide. What is the number of grams of acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) per c.c. of vinegar?

Calculation: A normal solution of sodium hydroxide NaOH contains 40 g. per liter. A solution of sodium hydroxide containing 5 g. in 100 c.c. or 50 g. in 1,000 c.c. is 50/40 normal (1.25 N). According to the rule, c.c. \times normality of acetic acid = c.c. \times normality of sodium hydroxide.

$$20 x = 13.8 \times 1.25$$

$$x = 0.862 \text{ (the normality of the acetic acid)}$$

A normal solution of acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, contains 60 g. per liter. An 0.862 normal acetic acid contains 0.862×60 or 51.72 g. per liter or 0.0517 g. per c.c.

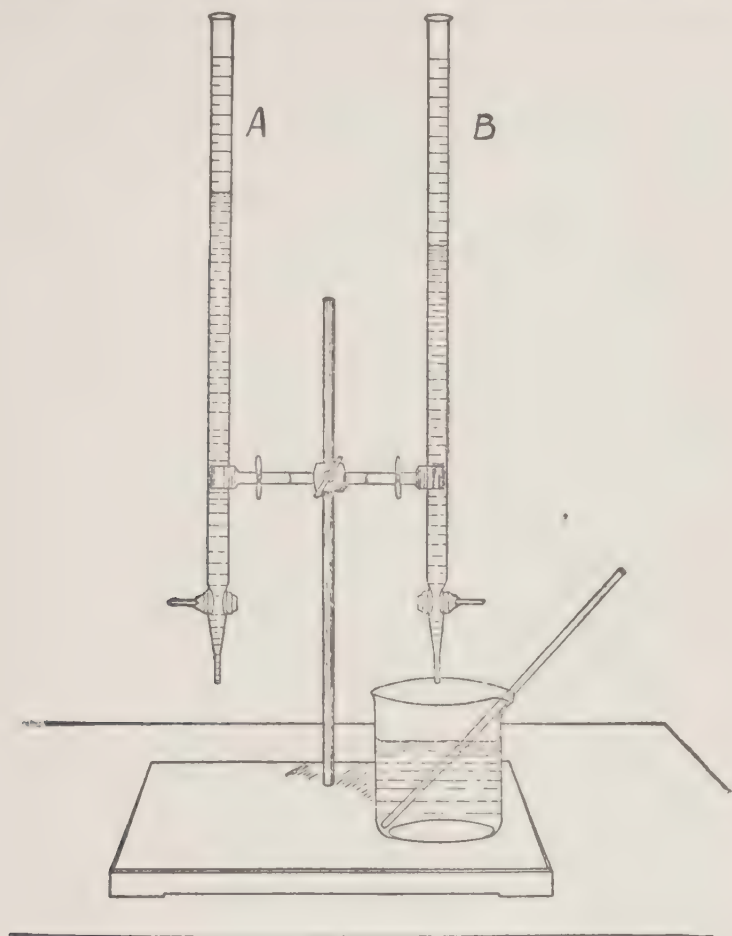


FIG. 20. Titration

QUESTIONS AND PROBLEMS

1. What are indicators? Name five indicators used in the laboratory and give the color of each in acid and in base. What plant colors may be used as indicators?
2. Distinguish between the terms, gram-molecular weight and gram-equivalent weight.
3. Distinguish between the terms, molar solution and normal solution. Give the advantages of expressing the concentration of a solution in terms of normality.

4. Fill in the blanks in the table:

<i>Solute</i>	<i>g. per l. of 1 molar soln.</i>	<i>g. per l. of 1 normal soln.</i>	<i>g. in 5 l. of 1 M. soln.</i>	<i>g. in 2 l. of 0.2 N. soln.</i>
Sulphuric acid				
Sodium hydroxide				
Nitric acid				
Sodium carbonate				

5. How many grams of hydrogen chloride are present in 300 c.c. of a twelve-molar solution of the acid?
6. How many grams of nitric acid are present in 450 c.c. of a five-molar solution of the acid?
7. (a) How many grams of sulphuric acid are present in 150 c.c. of a half-molar solution of the acid?
 (b) How many grams of zinc would react with the weight of acid obtained in (a)?
 (c) How many liters of hydrogen gas would be formed by reaction of the weight of acid obtained in (a) with zinc.
8. (a) How many grams of sodium hydroxide are present in 120 c.c. of a five-molar solution of sodium hydroxide?
 (b) How many grams of sodium hydrogen sulphate are formed when the weight of sodium hydroxide obtained in (a) reacts with sulphuric acid?
9. Calculate the normality of the following:
 - (a) a solution that contains 65.36 g. of phosphoric acid per liter
 - (b) a solution that contains 1.96 g. of phosphoric acid in 10 c.c.
 - (c) a solution that contains 2.45 g. of phosphoric acid in 250 c.c.
 - (d) a solution that contains 6 g. of acetic acid in 200 c.c.
 - (e) a solution that contains 19.6 g. of sulphuric acid in 50 c.c.
 - (f) a solution that contains 0.135 g. of oxalic acid in 10 c.c.
10. Calculate the number of grams of solute in each of the following solutions:
 - (a) 20 c.c. of 0.25 normal sulphuric acid
 - (b) 20 liters of 3 normal phosphoric acid
 - (c) 450 c.c. of 0.15 normal potassium hydroxide
 - (d) 8 c.c. of 6 normal sulphuric acid.

11. How many c.c. of 0.2 normal hydrochloric acid can be neutralized by 20 c.c. of 0.15 normal sodium hydroxide?
12. How many c.c. of 3 normal sodium carbonate solution will react with 80 c.c. of 0.1 normal sulphuric acid?
13. How many liters of 0.5 normal acetic acid will be required to neutralize 2 liters of 0.25 normal sodium hydroxide?
14. How many c.c. of 0.05 normal barium hydroxide solution will neutralize 50 c.c. of 0.12 normal nitric acid?
15. If in a titration 24 c.c. of a 0.5 N sodium hydroxide solution will neutralize 40 c.c. of a hydrochloric acid solution, what is the normality of the acid?
16. Calculate the normality of a solution of acetic acid from the fact that a volume of 42.5 c.c. of the acid is neutralized by 45.2 c.c. of a 0.2 N base. Express the concentration of the acid in grams per liter.
17. Calculate the normality of a solution of sodium carbonate from the fact that a volume of 36.4 c.c. is neutralized by 10 c.c. of 0.5 N acid. Determine the concentration of the sodium carbonate solution in grams per liter.
18. In a titration experiment to determine the concentration of acetic acid in vinegar, 100 c.c. of the vinegar required 15.6 c.c. of a 0.25 N solution of sodium hydroxide to neutralize it. Calculate the concentration of acetic acid in the vinegar in grams per 100 c.c.

CHAPTER XII

GRAPHIC REPRESENTATION OF VALENCE

Graphic Formulas. — We use diagrams or graphic formulas to represent the linkage of atoms in showing the construction of molecules. The valence of atoms is represented by bonds or links holding the atoms together, with the number of bonds leading from any atom equal to the valence of the element. Graphic formulas show merely the linkage of atoms and do not indicate which atoms give, take, or share electrons. In sodium chloride, written graphically as $\text{Na}—\text{Cl}$, the valence of sodium and chlorine each as one is represented by the single bond between the atoms.

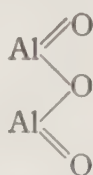
Calcium chloride, written as $\text{Ca} \begin{array}{l} \diagup \text{Cl} \\ \diagdown \text{Cl} \end{array}$, indicates that calcium is divalent (two bonds leading from calcium) and that chlorine is monovalent (one bond leading from the chlorine atom). Graphic formulas for a few other compounds are:



ammonia



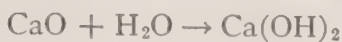
carbon disulphide



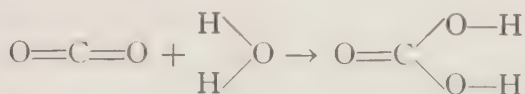
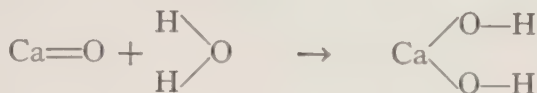
aluminium oxide

Anhydrides of Acids and Bases. — The use of graphic formulas makes possible a more complete understanding of the action of anhydrides of acids and bases with water (Chapter X).

We have learned that oxides of metals react with water to form bases, while oxides of non-metals react with water to form acids. Typical equations are:



The use of graphic formulas shows the valence of each atom as follows:

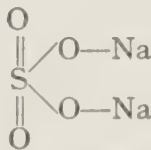
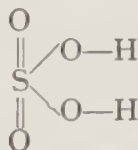
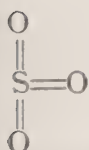
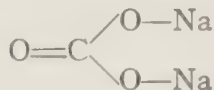
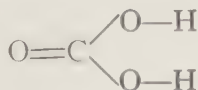
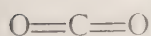


Note that the valence (as indicated by the number of valence bonds) of the metal and of the non-metal have not changed during these reactions.

An examination of the two graphic formulas $\text{Ca} \begin{array}{l} \diagup \text{O}-\text{H} \\ \diagdown \text{O}-\text{H} \end{array}$ and

$\text{O}=\text{C} \begin{array}{l} \diagup \text{O}-\text{H} \\ \diagdown \text{O}-\text{H} \end{array}$ shows the similarity between bases and acids.

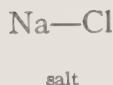
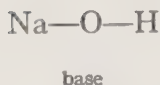
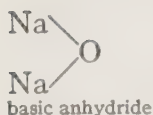
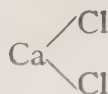
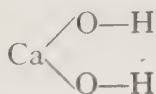
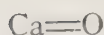
The first formula is the hydroxide of a metal (calcium), while the second is the hydroxide of a non-metal (carbon). In the latter compound (an acid), the hydrogen atoms may be displaced by an active metal to form a salt; in the former compound (a base), the hydroxide group is replaced by a negative radical to form a salt. That is, in the acid the link between the oxygen and hydrogen is disturbed or broken when the salt is formed; in the base the link between the metal and the oxygen is broken when the salt is formed. The relationship between the anhydride and the acid, base, or salt may be shown in the following graphic formulas:



acid anhydride

acid

salt



Types of Valence Bonds. — The relationship between valence and the structure of the atom has been discussed in Chapter VII, where it was shown that only the electrons in the outer orbit of an atom take part in a chemical reaction. In some compounds electrons may be transferred from one atom to another, as in the formation of sodium chloride and potassium iodide. In these compounds the atoms are said to be linked together by an **electrovalent bond**, and the compounds formed are often designated as electrolytes or polar compounds.¹ Typical electrovalent compounds exist as ions and not molecules since the electrons are transferred completely (Fig. 21). In other compounds, as carbon dioxide and ammonia, the electrons are not transferred, but are shared by the constituent atoms and there is no tendency for ions to be formed. These atoms are said to be held by a **covalent bond**, and the compounds formed are designated as non-polar compounds or non-electrolytes.²

Many compounds have been shown by experiment to have shared electrons or covalent linkage in the solid or gaseous form and to exist as ions when dissolved in water. Moreover, in other compounds the electrons are shared unequally by the constituent atoms so that part of the compound exists in the form of ions and part of it as molecules. Thus, it is evident that there is no sharper distinction between electrovalence and covalence than between tall and short people. While some compounds are

¹ The term **electrolyte** is based on the conductivity of the water solution of a compound, and **polar** means that one end of the molecule is positive and the other is negative. In almost all cases, however, the three terms — electrovalent, polar, and electrolyte — include the same compounds.

² As stated in the previous footnote, although these terms are not based on the same properties, in almost all cases they include the same compounds.

electrovalent and exist as ions, and other compounds have a typical covalent bond, there are many compounds in between these extremes.

It has been possible to learn much about the molecular, or ionic structure of substances by a process known as X-ray diffraction. When light rays are passed through a fine wire screen, they are bent or diffracted in such a way that definite patterns are formed. When the extremely short rays called X-rays are passed through a thin crystal, they are diffracted or bent in a similar way by the definitely arranged atoms or ions that make up the crystal. By the patterns formed from these X-rays scientists have been able to determine the arrangement of the atoms in the crystal. Extensive studies of this type have shown which solids exist as ions in crystals, or are electrovalent in structure, which compounds are covalent, and which are neither.

Electrovalence. — Acids, bases, and salts are the most typical examples of electrovalent or polar compounds. The formation of the salt, sodium chloride, by transfer of an electron from sodium to chlorine may be graphically represented as in Figure 21.

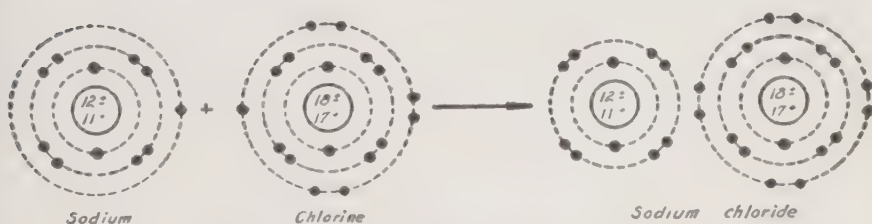
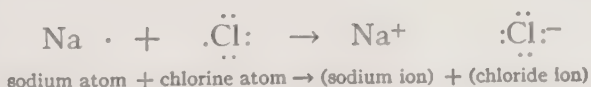


FIG. 21. Formation of Sodium Chloride

We may use only the electrons of the outer orbit to represent a reaction in which the transfer of electrons occurs, as shown by the following:



The X-ray diffraction pattern shows definitely that salts exist in crystal form as ions. The configuration of crystalline sodium chloride is represented in Figure 22. Note that the crystal consists of alternate sodium and chloride ions and that each sodium ion is surrounded by six chloride ions and each chloride ion is surrounded by six sodium ions. There are no definite sodium chloride molecules. Similar patterns have been made for other salts and for crystalline acids and bases. X-ray analysis shows that, even in crystals of a compound like calcium carbonate, the

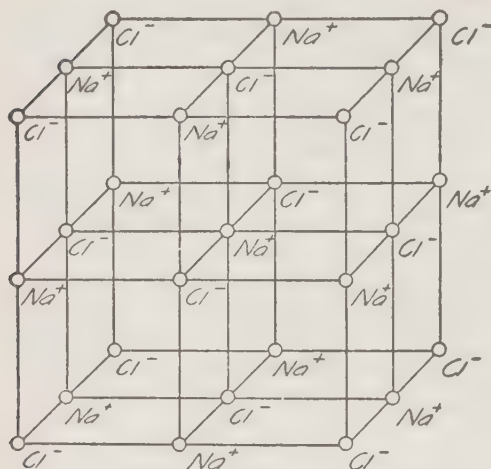


FIG. 22. Sodium Chloride Crystal

calcium ions alternate with groups of one carbon and three oxygen atoms — the carbonate ion.

Covalence. — Carbon dioxide is a typical compound with a covalent linkage in which carbon and oxygen contribute the shared electrons. Showing only the valence electrons in the outer orbit of the atoms, the reaction of carbon with oxygen may be represented as follows:



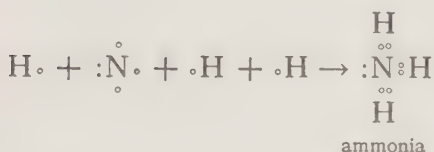
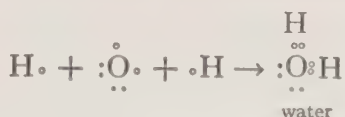
The electrons in the outer orbit of the carbon atom are shared with the valence electrons of the two oxygen atoms; each atom furnishes one electron of a pair which vibrates between the atoms of carbon and oxygen.

The X-ray analysis of frozen carbon dioxide (dry ice) indicates that each carbon atom is much closer to a pair of oxygen atoms than to other carbon atoms. In other words, this shows that

³ The circles are used to indicate shared electrons and the dots to represent other valence electrons.

carbon dioxide exists in solid form as molecules instead of as ions. Similar experiments have been made to show that other covalent compounds crystallize in the form of molecules.

Examples of other compounds whose molecules are held together by covalent bonds may be represented as follows:



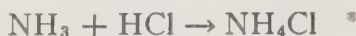
There is no transfer of electrons (and therefore no ions) in molecules held together by covalent bonds. However, as the electrons vibrate, one atom may have a greater tendency to attract electrons than another atom — the atoms that attract electrons have an apparent negative valence and the atoms from which electrons are attracted have an apparent positive valence (Chapter VII).

The linkages of atoms to form molecules of elements may also be explained by covalent bonds. In hydrogen molecules, each atom furnishes one of a pair of shared electrons as represented by $\text{H}:\text{H}$. Chlorine molecules and oxygen molecules are represented by the diagrams:

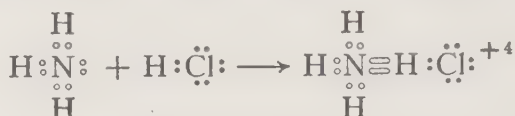


Coördinate Valence. — The method by which neutral compounds combine with each other may be explained by a third type of valence known as coördinate valence. This type of combination may take place when *one atom* in a compound can furnish one or more pairs of electrons, to be shared with another atom. An important reaction studied in the laboratory is the combination of invisible ammonia gas with invisible hydrogen chloride

gas to form a white cloud — the salt, ammonium chloride. The equation for the reaction is:



Showing the valence electrons, the equation may be written:



The hydrogen ion (H^+) of hydrogen chloride gas has no electron in its outside orbit; the nitrogen atom of ammonia gas has two unshared electrons which it shares with the hydrogen atom in a coördinate valence linkage; the complex ammonium radical (NH_3 and H^+) then assumes a positive charge, while the chloride remains a negative ion. In other words, the resulting compound, ammonium chloride, NH_4Cl , is a polar compound.

QUESTIONS AND PROBLEMS

1. Write the following as graphic formulas: Mn_2O_7 , CrO_3 , Sb_2S_3 , P_2O_5 , CCl_4 , SnO_2 , Na_3N , ZnBr_2 , Mg_3N_2 , SiC .
2. Define the terms: acid anhydride; basic anhydride. Give formulas for three compounds of each kind; write each as graphic formulas.
3. Using the following acids, write the graphic formula for the acid, for the acid anhydride, and for the normal sodium salt of the acid: sulphurous acid; carbonic acid; chloric acid.
4. Using the following bases, write the graphic formula for the base, for the basic anhydride, and for the chloride of the metal: magnesium hydroxide; aluminium hydroxide; potassium hydroxide.
5. Use the valence electrons of calcium and chlorine atoms to show how the electrovalent compound, calcium chloride, is formed. Explain the electron transfer.
6. Use the valence electrons to show how nitrogen combines with hydrogen in a covalent linkage to form ammonia. How many pairs of electrons are shared? Which element is essentially positive? Which is essentially negative?

⁴ Circles represent the shared electrons of nitrogen and hydrogen atoms in ammonia and those that are to be shared by the hydrogen atom of HCl . The oval bonds represent coördinate valence, the two electrons of nitrogen being shared with the hydrogen of HCl .

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CHAPTER XIII

PROPERTIES OF SOLUTIONS. THE IONIZATION THEORY

Need of a Theory. — For many years, scientists have pondered over the action of acids, bases, and salts because they do not behave like other compounds when in water solution. Some of the more important differences are expressed in the following paragraphs:

1. Acids, bases, and salts show their characteristic reactions only when in water solution. Dry solid acids and bases have no effect on litmus or other indicators; solid acids will not react with baking soda.
2. Pure water, or a solution of sugar in water, does not conduct the electric current, while a solution of an acid, base, or salt conducts electricity.
3. A solution containing one gram-molecular weight of sugar, glycerin, or alcohol, in 1,000 grams of water, will freeze at -1.86°C . and will boil at 100.52°C . A similar solution of any acid, base, or salt has a lower freezing-point and a higher boiling-point than those of sugar, glycerin, or alcohol.
4. When a direct current of electricity is passed through a solution of an acid, base, or salt, a chemical change takes place.
5. Acids, bases, and salts in water solution interact almost instantaneously while reactions of sugar, glycerin, and similar substances, whether dry or in water solution, undergo reaction slowly.

It was from 1883 to 1887 that many of these properties were partially explained by the **theory of ionization**, formulated by **Arrhenius**. This theory may be given in one brief statement: Molecules of acids, bases, and salts, when dissolved in water, tend to separate or ionize into two or more electrically charged parts, called ions. At the time of Arrhenius, the electrical structure of matter had not been suggested; nor had it been

possible to show that many compounds exist in crystal form as ions. It is remarkable that, with the information then available, a theory so near the truth could have been devised. Arrhenius thought of ions as existing only in water solution because they were more evident in this state; the compounds which Arrhenius studied are now classed as typical electrovalent compounds or electrolytes, many of which exist normally as ions in the solid or liquid (fused) state, as well as in water. In crystalline form the ions are not free to move, and it is difficult to study these substances at the high temperatures necessary for obtaining them in the fused state; consequently we shall study the characteristics of acids, bases, and salts (electrolytes) just as Arrhenius did — in water solution in which they exist as ions in motion.

Acids and Bases in Terms of Ions. — An acid was defined (Chapter X) as a compound in which the hydrogen may be displaced by certain active metals. As acids dissolve in water, the hydrogen ions are free to act; it is the presence of the hydrogen ions in all acid solutions that give them their characteristic properties — sour taste, ability to change blue litmus to pink, and the ability to react with metals and baking soda. Therefore an acid may be considered as an electrolyte which in water solution forms hydrogen ions. Similarly, solutions of bases contain hydroxide ions which give bases their characteristic properties — alkaline taste, ability to change pink litmus to blue and to neutralize acids. A base may be considered as an electrolyte which in water solution forms hydroxide ions.

Conductivity of Solutions. — A conductivity apparatus (Fig. 23) is a device used to determine whether or not a substance will conduct an electric current. The apparatus shown is used to study substances in solution. Two wires connected through a light bulb to a source of electricity are dipped into the solution to be tested. If the wires are dipped into a water solution of an acid, base, or salt (electrolyte) where ions are present, the positive ions will be attracted to the negative electrode and the negative ions will be attracted to the positive electrode. In this way, the solu-

tion will conduct the current, the electric circuit will be closed, and the lamp will glow. If the wires are dipped into pure water, or into a solution of sugar (a non-electrolyte), or in contact with any kind of a dry crystal, there will be no free ions to act as conductors and hence the lamp will not glow.

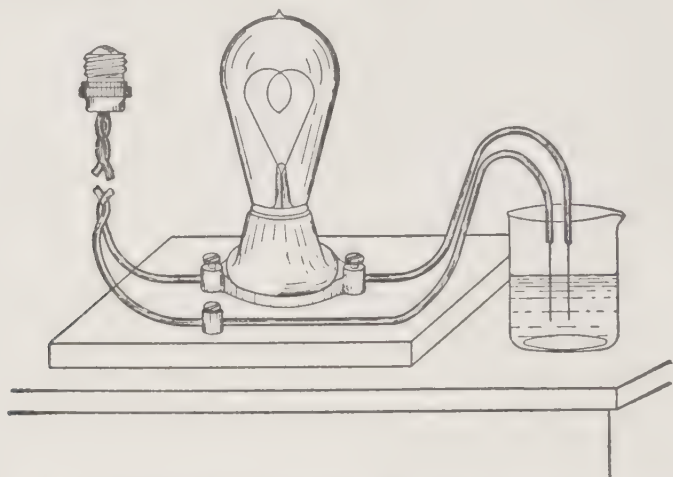


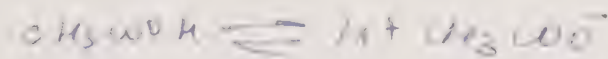
FIG. 23. Apparatus for Indicating the Conductivity of Solutions

When solutions of different electrolytes are tested in this way, the lamp glows more brightly for some solutions than for others, indicating a stronger conductivity or a greater concentration of freely moving ions. Thus the conductivity apparatus may be used not only to determine whether a substance in solution is an electrolyte or a non-electrolyte, but also to determine the relative concentration or activity of the ions present to carry the current. Accurate methods have been devised with which it is possible to determine the exact conductivity of a solution and from this, to calculate the concentration of freely moving ions.

Strong Electrolytes. Weak Electrolytes. — According to a theory devised by Debye and Hückel, some compounds are completely ionized in dilute solution. It would be expected that, when a crystal of sodium chloride dissolves in water, the positively

charged sodium ions and the negatively charged chloride ions would separate and move about independently in the water. On the other hand, experiments show that the conductivity of these electrolytes in solution is less than would be expected if all the solute were present as freely moving ions. The Debye-Hückel theory explains this fact by considering that the ions are not freely moving but are retarded by interionic attraction. In other words, the electrolytes have a lower conductivity because the attraction between the oppositely charged ions retards their movement through the solution. This is especially true in concentrated solutions where the ions are closer together and where some ions may combine to form molecules. Compounds which are completely ionized in dilute solution are called **strong electrolytes**. They include practically all salts. The only familiar acids that are strong electrolytes are hydrochloric, nitric, and sulphuric; and the strongest of the familiar bases are potassium hydroxide and sodium hydroxide.

The conductivity of nearly all of the acids and bases not listed as strong electrolytes is so low that it can only be explained by the theory that a substantial proportion of the solute (weak electrolyte) exists in the form of molecules and only a portion of each exists as ions. Thus weak electrolytes behave according to the theory of Arrhenius — they exist as molecules before being dissolved in water; and in solution there is a tendency for the molecules to dissociate into ions. As weak electrolytes ionize, many of the ions in solution again unite as molecules because there is a greater attraction between the ions of weak electrolytes than with strong electrolytes. In other words, two opposing reactions are taking place constantly in a solution of a weak electrolyte — dissociation of molecules into ions and association of ions to form molecules. After a time the two reactions are occurring at the same rate and there is said to be a condition of equilibrium. Reactions of this type are said to be reversible and many illustrations will be encountered in later chapters. Using acetic acid as an example, the opposing reactions may be written as follows:



Solutions of strong acids and bases differ from the weak electrolytes not only in conductivity but by the intensity of other properties. That is, the high concentration of hydrogen ions even in dilute solutions of strong acids causes them to be very sour to the taste, and to react vigorously with baking soda, bases, and metals; weak acids in comparison are mild in taste, and react slowly with baking soda, bases, and metals. We use vinegar in foods for its sour taste; if the foods were flavored with hydrochloric acid, it would have to be used much more sparingly to avoid an excess of hydrogen ions (or sourness). Strong bases, because of the high concentration of hydroxide ions, are not only excellent conductors of electricity, but are decidedly caustic and corrosive and react readily with acids and with proteins. Thus solutions of lye (sodium hydroxide, a strong electrolyte) are much more effective in cleaning than ammonia water (ammonium hydroxide, a weak electrolyte) but must be used with greater caution.

Boiling-Point and Freezing-Point of Solutions. — The effect of solute upon the boiling-point of a solution may be described with reference to Figure 24. In one beaker the circles represent molecules of water, which in liquid form are in continual motion. As the liquid is heated, the molecules move more and more rapidly and the vapor tension increases as particles leave the surface of the liquid, until the boiling-point is reached (Chapter VIII). In another beaker, the crosses represent molecules or ions of a solute mixed with water molecules (circles). We could imagine that the solute particles would interfere with the movement of the water molecules and lower the rate at which they leave the surface of the liquid; by heating the solution to a higher temperature, the vapor tension increases until a new boiling-point is reached, higher than that of pure water. In other words, the temperature at which the vapor tension exceeds the atmospheric pressure (boiling-point) is higher for any solution than it is for pure water. We have a familiar illustration of this in the boiling temperature of syrups and jellies, which, as we know, is much higher than that of water.

A similar explanation could be given to show that molecules or

ions of a solute have a tendency to depress the freezing-point (Chapter VIII) of a solution. It is a well-known practice to add alcohol or a "freezing mixture" to the water in an automobile radiator in winter. Water freezes at 0°C . with damage to the container (if closed), while a mixture of some solute with the water will still be a liquid at 0°C . and will not become solid until a temperature several degrees colder has been reached.

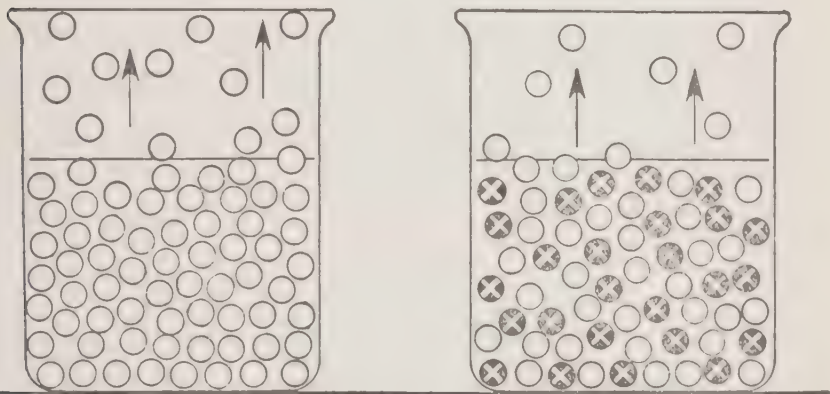


FIG. 24. Effect of Solute upon the Boiling-Point of a Solution

Experimental work has shown that if we have the same number of molecules of many different non-electrolytes in 1,000 g. of water, the increase in boiling-point and the lowering of freezing-point is exactly the same. A general statement is: When a gram-molecular weight (6.06×10^{23} molecules) of a non-electrolyte is dissolved in 1,000 g. of water, the boiling-point is raised by 0.52° and the freezing-point is lowered by 1.86° . Half as many molecules ($1/2$ g.m.w.) would change the boiling-point by 0.26° and the freezing-point by 0.93° , or twice as many molecules (2 g.m.w.) would affect the boiling-point by 1.04° and the freezing-point by 3.72° . This is illustrated in Table XI.

When electrolytes dissolve in water, each ion has the effect of a molecule in raising the boiling-point and lowering the freezing-point. If one gram-molecular weight of sodium chloride is dissolved in 1,000 grams of water, the resulting solution will contain

TABLE XI

BOILING-POINT AND FREEZING-POINT OF SOLUTIONS OF NON-ELECTROLYTES
(expressed as no. of g.m.w. per 1,000 g. water)

<i>Substance</i>	<i>Boiling-Point</i>	<i>Freezing-Point</i>
Water	100.00° C.	0° C.
Sugar (1 g.m.w.)	100.52°	-1.86°
Sugar (0.5 g.m.w.)	100.26°	-0.93°
Glycerin (1 g.m.w.)	100.52°	-1.86°

$2 \times 6.06 \times 10^{23}$ ions (instead of 6.06×10^{23} molecules). The calculated boiling-point of the solution would be $100^\circ + (1 \times 2 \times .52) = 101.04^\circ$ C. and the freezing-point would be $0^\circ - (1 \times 2 \times 1.86) = -3.72^\circ$ C. (Table XII).

TABLE XII

CALCULATED BOILING-POINT AND FREEZING-POINT OF SOLUTIONS OF
STRONG ELECTROLYTES (expressed as no. of g.m.w. per 1,000 g. water)

<i>Substance</i>	<i>Boiling-Point</i>	<i>Freezing-Point</i>
NaCl (1 g.m.w.)	101.04	-3.72
NaCl (2 g.m.w.)	102.08	-7.44
CaCl ₂ (1 g.m.w.)	101.56	-5.58
CaCl ₂ (0.5 g.m.w.)	100.78	-2.79

When the boiling-points and freezing-points of these solutions are determined experimentally, the boiling-point is slightly lower and the freezing-point is slightly higher than the values in Table XII. If the solutions are more concentrated than those indicated in the table, the deviation from the calculated value is greater. The Debye-Hückel theory states that the interionic attraction between the oppositely charged ions which causes a lower conductivity than that obtained from a completely ionized solute, also reduces the effect of the ions on the vapor pressure; as a result the change in the boiling-point and freezing-point is reduced. When the solutions are concentrated, the interionic attraction is more pronounced and the deviation of the experimental boiling-

point and freezing-point from the calculated value is even greater.

In summary, we may say that, if we disregard interionic attraction, each gram-molecular weight of ions or molecules (6.06×10^{23} particles) dissolved in 1,000 grams of water raises the boiling-point by 0.52°C . and lowers the freezing-point by 1.86°C . With non-electrolytes, the number of particles (all molecules) is determined by the number of gram-molecular weights of solute dissolved in 1,000 grams of water. With strong electrolytes, the number of particles (all ions) is determined by the number of gram-molecular weights of solute dissolved and by the number of ions formed by each molecule. With weak electrolytes, the number of particles (ions and molecules) is dependent on the same factors as for strong electrolytes and also on the percentage of ionization.

Experimental Determination of Gram-Molecular Weight of Non-Electrolytes. — Equipment is available for the accurate determination of boiling-point and freezing-point of solutions. The data obtained may be used to determine the gram-molecular weight of a non-electrolyte that is dissolved in water. That is, re-stating the rule given at the first of the chapter, the weight of a non-electrolyte which, when dissolved in 1,000 g. of water, raises the boiling-point by 0.52°C . or lowers the freezing-point by 1.86°C . is the gram-molecular weight of the compound. The following problems illustrate the method of calculation.

Problem: A laboratory experiment showed that 90 g. of a non-electrolyte dissolved in 1,000 g. of water gave a boiling-point of 100.26° . What is the gram-molecular weight of the compound?

Calculation: The rise of boiling-point, 0.26°C ., is one-half of the normal rise of boiling-point for one gram-molecular weight of non-electrolyte per 1,000 g. of water. Therefore, it would require 2×90 g. of this non-electrolyte to give a boiling-point of 100.52°C . Consequently the gram-molecular weight is 180 g.

Problem: Calculate the gram-molecular weight of alcohol from the data that 11.5 g. of it per 1,000 g. of water gives a freezing-point of -0.465°C .

Calculation: A proportion may be used to show the relationship of solute (non-electrolyte) dissolved to the lowering of the freezing-point:

$$11.5 \text{ g.} : 0.465^{\circ} :: x : 1.86^{\circ}$$

$$x = \frac{11.5 \times 1.86}{0.465}$$

$$x = 46 \text{ g.}$$

Forty-six grams is the weight of alcohol which, if dissolved in 1,000 g. of water, will lower the freezing-point by 1.86°C . Therefore, 46 g. is the gram-molecular weight of alcohol.

In daily life there are many applications of the effect of the solute upon the boiling- and freezing-points of solutions. We are familiar with the use of salt in freezing mixtures. It is evident that pure ice would be useless in freezing ice-cream because the custard to be frozen is a solution with a lower freezing-point than water. Salt is added to the ice until a solution forms which has a lower freezing-point than the ice-cream mixture. If there is a high concentration of acid (fruit juices) or sugar in the custard, it will have a still lower freezing-point. A similar application of the same principle is the addition of alcohol, glycerin, or other compounds to the water in automobile radiators in order to lower the freezing-point of the mixture below that indicated by the weather conditions. Again, another unusual application has been made of the lowering of the freezing-point in detecting the adulteration of milk with water. The concentration of dissolved solids in milk is so constant that the freezing-point of milk from different sources is always the same. If water is added to it, however, the solution becomes more dilute and the freezing-point of milk detects the adulteration.

Electrolysis and Electroplating. — We have learned that water solutions of electrolytes are conductors of electricity, and we assume that this conductivity is caused by the presence of positively and negatively charged ions in the solution. If a direct current is passed through the solution, there is a tendency for the positively charged ions to migrate to the negative electrode and

for the negatively charged ions to migrate to the positive electrode. The positive ions are known as **cations** and the negative electrode to which they migrate is the **cathode**; the negative ions are known as **anions**, and the positive electrode to which they migrate is the **anode**. The charged particles do not remain as ions when they collect in this way at the cathode and anode. If the electrolyte is hydrochloric acid in water solution, the positive hydrogen ions will collect at the negative electrode and each will receive an electron from it. The result is the formation of hydrogen atoms which in turn form molecules of hydrogen gas. The negative chloride ions collect at the positive electrode and discharge their electrons, forming chlorine atoms which unite to form molecules of chlorine gas. This process of decomposing a compound by the electric current through the action of the ions is called **electrolysis**.

The process of electrolysis is a practical method for preparing many of the elements in pure condition. For example, the electrolysis of water has been mentioned (Chapters IV and VI) as one of the commercial methods for the preparation of hydrogen and oxygen. Again, it is known that pure metals may be obtained at the cathode when the electric current is passed through a water solution of the salt. Many of the reactive metals such as sodium and potassium can be separated from their compounds only by electrolysis of the fused (melted) salt or hydroxide. Aluminium was much too expensive to use for kitchen utensils until the chemist perfected a method for separating it from aluminium oxide by electrolysis.

The process of electroplating is an application of electrolysis. Expensive metals such as gold, silver, chromium, and nickel are plated on comparatively inexpensive metals to enhance their beauty and protect them from corrosion. In the diagram (Fig. 25) the process of silver-plating spoons is illustrated. The spoons are made the cathode by attaching them to the negative terminal C; the anode consists of bars of silver which are attached to the positive terminal A. The apparatus is filled with a solution of silver salt. When a current of electricity is passed through the solution, the silver ions are attracted to the cathode, where they add an

electron and are deposited as pure silver on the spoons. The negative radicals are attracted to the anode, where they combine with

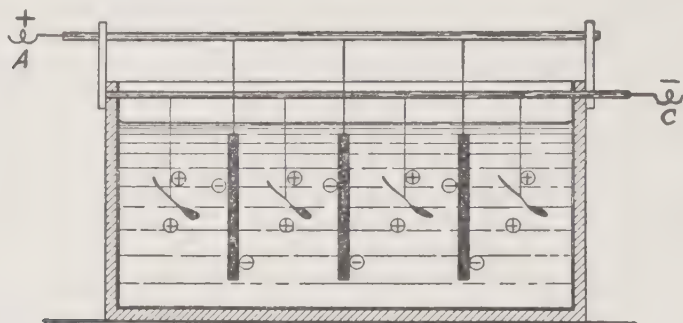


FIG. 25. Electroplating Spoons

silver from the silver bars and hence a silver salt goes into solution. Thus silver is constantly dissolved from the silver bars and deposited on the spoons.

Modern Conceptions of Acids, Bases, and Salts. — The definitions of the terms acids, bases, and salts which have been given in the preceding chapters are typical of the conceptions regarding them that have been satisfactory for years. Recently, in order to account for similar reactions of compounds, including those in solvents other than water, the scientist Brönsted has developed broader and more inclusive definitions of acids, bases, and salts. At first glance, Brönsted's definitions do not appear to differ greatly from those we have learned. An acid is defined as a substance which gives up protons (another term for hydrogen ions) and a base as a substance which accepts protons. The difference becomes evident when we realize that the acids do not necessarily need to be in water solution to give up the protons, but may be either undissolved or dissolved in some other solvent. Moreover, it is known that protons do not exist in water as hydrogen ions, but instead combine with water molecules to form complex ions H_3O^+ , known as **hydronium** ions; thus the reaction of hydrogen chloride gas with water may be written:



When these facts are considered, the word acid includes all substances formerly called acids and in addition, the following:

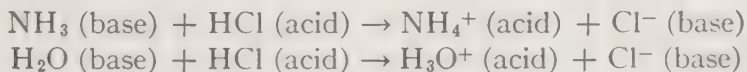
- (a) the hydronium (H_3O^+) ions and ammonium (NH_4^+) ions.
- (b) the negatively charged radicals that contain replaceable hydrogen, as HCO_3^- and HSO_4^-
- (c) water.

Similarly, the term base includes the hydroxides of metals and also the following:

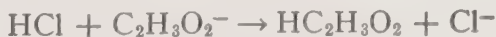
- (a) all negatively charged ions (anions)
- (b) water and ammonia
- (c) solvents that combine with protons.

According to this conception, water and acid anions may act as acids and as bases. Water is an acid when it gives up a proton (H^+), leaving the hydroxide ion (OH^-) and is a base when it combines with a proton to form the hydronium ion (H_3O^+). The anions from acid salts (HCO_3^- and HSO_4^-) act as acids when they give protons and become $\text{CO}_3^{=}$ and $\text{SO}_4^{=}$ ions, and as bases when they accept protons to form H_2SO_4 and H_2CO_3 .

These definitions may be applied to the compounds when they react without water; for example, the reaction of ammonia gas with hydrogen chloride gas is similar to the reaction of water with hydrogen chloride gas, as shown by the equations:



Applying the Brönsted theory to solvents other than water, we may study a reaction in which glacial (100 per cent) acetic acid is the solvent. In acetic acid as a solvent, hydrogen chloride is neutralized by sodium acetate in the same way that hydrogen chloride reacts with sodium hydroxide in water, by neutralization. In glacial acetic acid, the molecules of HCl give protons (hydrogen ions) to the acetate ions of sodium acetate, thus reducing the concentration of available protons and neutralizing the solution as indicated by the equation:



Practically all of the reactions with which we are concerned take place in water solution, and for this reason we will find only occasional applications of the Brönsted theory.

QUESTIONS AND PROBLEMS

1. State the theory of ionization as formulated by Arrhenius.
2. Explain the following terms and give an example of each: electrolyte, non-electrolyte, strong acid, strong base, weak acid, weak base, a polar compound.
3. List three ways in which solutions of electrolytes differ from solutions of non-electrolytes.
4. Write equations to show the equilibria between ions and molecules in water solutions of the following weak electrolytes: ammonium hydroxide, acetic acid, carbonic acid, hydrosulphuric acid, magnesium hydroxide.
5. Fill in the blanks of the following table:

	<i>34.2 g. sugar (C₁₂H₂₂O₁₁) in 1,000 g. of water</i>	<i>684 g. sugar (C₁₂H₂₂O₁₁) in 1,000 g. of water</i>
Number of molecules in the solution		
Boiling-point of solution		
Freezing-point of solution		

6. Fill in the blanks of the following table (assume complete ionization of the salts):

	<i>1 g.m.w. Ca(NO₃)₂ in 1,000 g. water</i>	<i>0.2 g.m.w. NaCl in 1,000 g. water</i>
Number of ions in the solution		
Boiling-point of solution		
Freezing-point of solution		

7. A solution containing ten grams of a non-electrolyte in 1,000 g. of water has a freezing-point of -0.202° C. Use the data to determine the gram-molecular weight. The compound is glycerol, C₃H₅(OH)₃. Use the formula to determine the gram-molecular weight.

8. Describe the conductivity apparatus, and tell how it is used to distinguish between an electrolyte and a non-electrolyte, and between a weak and a strong electrolyte.
9. Distinguish between the terms strong acid and concentrated acid, and between weak acid and dilute acid.
10. Discuss the comparative advantages of lye and ammonia water for cleaning in the home.
11. Why do solutions of all copper salts have a blue color?
12. Diagram and describe the method by which spoons are plated with silver.
13. Explain the terms acid and base according to the Brönsted theory. According to this theory, explain how the following substances act as acids: water, ammonium ion, HCO_3^- ion; explain how the following substances act as bases: water, SO_4^{2-} ion, ammonia.

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CHAPTER XIV

TYPES OF REACTION. FACTORS INFLUENCING REACTIONS

THE reactions encountered throughout the study of chemistry are more easily remembered when we think of them in terms of certain characteristic types of reaction. Each reaction is not to be considered as a separate problem but as one of a group of similar reactions. A classification of a few important types of reaction is given in Chapter VI. These include decomposition, combination, and displacement reactions. Double decomposition reactions were mentioned in Chapter VII. The theory of ionization gives important conceptions of the properties of the substances taking part in these reactions, and it is necessary to review the reactions in the light of the information which has been gained.

Displacement Reactions. — The ionization theory helps us to understand reactions in which one element displaces another in a compound. A typical reaction of this type is the displacement of hydrogen from sulphuric acid by zinc, as shown by the equation:



In this reaction the metal zinc is added to the sulphuric acid in solution which we have learned is in the form of ions:



Experiments have shown that zinc atoms have a greater tendency than hydrogen atoms to give electrons. (In former chapters zinc was said to be more "active" than hydrogen.) Consequently, the hydrogen ions of the acid solution take electrons from the zinc atoms, forming molecules of hydrogen (H_2) and zinc ions. Since the sulphate ions are not affected, the only chemical change in the

solution is the transfer of electrons from zinc atoms to hydrogen ions, as indicated in the following ionic equation:



Since hydrogen ions are characteristic of all acids in solution, it follows that the same ionic equation could be written for the reaction of zinc with any acid. The negative ion of the acid is concerned with the reaction only when the water of the solution is evaporated; then the negative ion of the acid crystallizes with zinc ion to form a salt.

Electrochemical series

Potassium
Sodium
Calcium
Magnesium
Aluminium
Manganese
Zinc
Chromium
Iron
Nickel
Tin
Lead
Hydrogen
Antimony
Bismuth
Copper
Mercury
Silver
Platinum
Gold

In Chapter VI we learned that the metals and hydrogen may be arranged in a list called the electrochemical series. As shown in the foregoing paragraph, the metals preceding hydrogen in the series have more tendency to give up electrons than hydrogen atoms have. Consequently, dilute acids will react with the metals preceding hydrogen in the series. The metal gives up electrons and thus passes into ionic form; the electrons are accepted by hydrogen ions, and molecules of hydrogen gas are formed. Metals below hydrogen in the series have no tendency to give up electrons to hydrogen ions and so are not attacked by dilute acids.

The electro chemical series is an arrangement which shows the relative ease with which all the positive elements give up electrons to form ions. Potassium is a very active element and gives up electrons to any element below it in the list and so displaces any of these metals from their compounds. The other metals will displace any positive element below them in the series. If iron nails are placed in a solution of a copper salt, the iron is dissolved readily, while the copper precipitates. This reaction is easily followed by the disappearance of the blue color of the copper ions and the formation of the red-

brown precipitate of metallic copper. The equation may be written as follows:

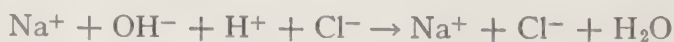


Since the sulphate ion is not affected in this reaction, the ionic form of the equation is:



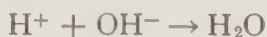
A knowledge of the electrochemical series is important when we use aluminium cooking utensils. The fact that aluminium precedes iron in the electrochemical series means that it will displace iron from its compounds. Thus when spinach or other green-leaf vegetables rich in iron (which is desirable in the food) are cooked in aluminium vessels, there is a tendency for the iron to be displaced by the aluminium. Moreover, the displaced iron precipitates as an undesirable black deposit on the sides of the pan. When acid foods are cooked in the same utensil the deposit of iron as well as the surface of the aluminium pan may be dissolved by the acid food and thus the pan will become bright again.

Double Decomposition Reactions. — Whenever solutions of electrolytes are mixed, a reaction appears to take place instantly without the application of heat or any of the other factors so necessary to the success of many reactions. The instantaneous reaction between acids, bases, and salts may be explained by the ionic theory. Strong electrolytes in solution are in the form of ions. When the solutions are mixed, a reaction occurs immediately, for it is only necessary that the ions of opposite charge unite. The neutralization of sodium hydroxide with hydrochloric acid may be indicated as follows to illustrate a double decomposition reaction:



When the two solutions are allowed to react, the only change that takes place in the mixture is the uniting of the oppositely charged ions. Moreover, we know that in dilute solutions the sodium and chlorine ions do not combine to any extent, since the salt, sodium

chloride, is in the form of ions. Consequently the only chemical change that takes place when the acid and base are mixed is the uniting of the H^+ and OH^- ions to form water. The ionic equation representing the reaction is

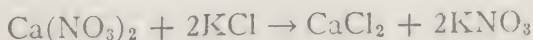


Since all acids in solution contain hydrogen ions and all bases in solution contain hydroxide ions, the same ionic equation would apply to any neutralization equation. This fact is confirmed by the evidence that the heat evolved in any neutralization reaction between highly ionized electrolytes depends only on the amount of water formed and not on the type of acid and base involved. The positive ion of the base and the negative ion of the acid do not enter into the reaction until the neutral solution is evaporated; then these ions crystallize in the form of a salt, the nature of which depends on the acid and base used.

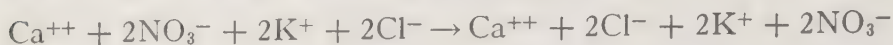
In Chapter XIII we learned that when solutions of acids, bases, or salts (electrolytes) react by double decomposition, the reaction takes place instantaneously without the application of heat or any other form of energy. This is possible because the substances are in the form of ions in the solution and all that occurs is that the ions of opposite charge meet and unite. In the neutralization reactions the hydrogen and hydroxide ions need only to meet in the solution for the reaction to take place.

Reversible double decomposition reactions. — In the neutralization of sodium hydroxide with hydrochloric acid it was noted that the sodium and chlorine ions did not unite, because of their tendency to exist as ions. The hydrogen and hydroxide ions reacted only because they formed an unionized compound.

If we should study double decomposition reactions in which water is not a product we will find many instances in which both products exist as ions and thus no actual change can take place. In the following reaction written in molecular form:



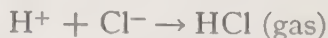
we have four soluble salts that exist in solution as ions. To show the ions reacting, the equation would be written:



A study of such a reaction will show that when the solutions are mixed the ions do not combine or change in any way. If the water is evaporated from the mixture to form crystalline salts, the calcium ions will unite with both types of negative ions to form both calcium nitrate and calcium chloride. At the same time the potassium ions will form both potassium nitrate and potassium chloride crystals. The result is a mixture of the four salts. A reaction of this type in which the products may react to form the original substances is called a **reversible reaction**. As a rule they are of little value in the laboratory because only a mixture of substances result. Occasionally, by applying the mass law, which will be studied soon, it is possible to manipulate these mixtures to obtain a pure salt.

Double Decomposition Reactions that Go to Completion. — In contrast to the reversible reaction just studied, **neutralization reactions** are said to continue to completion because the union of the hydrogen ions with the hydroxide ions removes these from the solution, thus preventing the ions from interacting to form the original substances. This type of reaction results in the formation of a pure salt and is valuable in the laboratory. In general, double decomposition reactions will go to completion whenever **one of the products can be removed from the solution**. This is usually accomplished in one of three ways:

1. A gas may be formed and removed from the other products of the reaction. In the laboratory, hydrogen chloride gas is prepared by the reaction of sulphuric acid to furnish H^+ ion and sodium chloride to furnish Cl^- ion. The ionic equation is:



Because the hydrogen chloride gas is soluble in water, it does not separate as a gas until the mixture is heated. While any chloride may be used to furnish Cl^- ion, acids of low boiling-points are

unsatisfactory as a source of H^+ ion because they tend to vaporize with the hydrogen chloride. Sulphuric acid is one of the few acids that may be used; it has a high boiling-point and will not change to a gas until all of the hydrogen chloride has separated. With the proportion of reactants and the methods used in the laboratory, the equation for the reaction is:

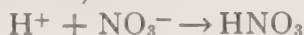


As the mixture is heated, the hydrogen chloride gas is continually removed and thus any reversible reaction with the sodium hydrogen sulphate is impossible.

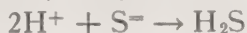
Nitric acid is a low boiling-point acid which under certain conditions may be evolved as a gas; it is prepared by heating a mixture of any nitrate with an acid that has a high boiling-point. Sulphuric acid is usually used because it is the most available of any of the high boiling-point acids. An equation for the preparation of nitric acid follows:



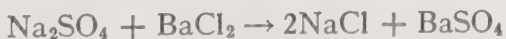
The reaction, in ionic form, is:



Other gases that may be formed to cause a reaction to go to completion are CO_2 (from H_2CO_3), H_2S , and NH_3 (from NH_4OH). When any of these gases form in a reaction, they are evolved at room temperature. For this reason, any reaction in which they are formed will go to completion. The ionic equations for their formation are:



2. An insoluble precipitate may be formed, as in the reaction:



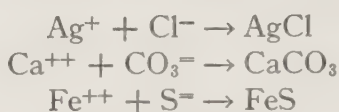
Whenever a solution of any sulphate reacts with a solution of a barium salt, the barium sulphate precipitates as a white insoluble

salt. This removes the Ba^{++} and the SO_4^- ions from solution and thus prevents any reaction with the ions of the other product. Since the Na^+ and the Cl^- ions in the reaction are not affected, the only chemical change is represented by the equation:



Three other insoluble salts that are useful in the laboratory to cause reactions to go to completion are silver chloride (AgCl), calcium carbonate (CaCO_3), and iron sulphide (FeS).

The ionic equations for the formation of these precipitates are:



3. **A slightly ionized substance may be formed.**—Neutralization reactions are the most important of this type, because water is always one of the products in these reactions. Water is one of the common slightly ionized substances used to cause a reaction to go to completion, though in some cases weak acids and bases may act in this way.

Factors Which Influence Reversible Reactions. The Mass Law. — We may emphasize again that in a reversible reaction at equilibrium, the products of the reaction are forming the initial reactants at the same rate that they are being formed by these reactants. As a result, the concentration of each constituent remains the same as long as there is no change in the conditions that affect the rate of the reaction in either direction. Because so many chemical reactions have a tendency to be reversible and to form equilibrium mixtures, it is important to study the factors that affect these reactions. In Chapter IV, attention was directed to the fact that the speed of an oxidation reaction is influenced by (1) temperature, (2) catalysis, and (3) concentration of reacting substances. In a similar way, these factors may be considered to influence the rate of all chemical reactions. The effect of temperature and of catalytic agents is principally that of accelerators to overcome certain factors which tend to retard the reaction. Thus

hydrogen and oxygen under ordinary conditions do not unite to form water, but when raised to a high temperature or in the presence of certain catalytic agents they combine easily.

The equilibria between the two reactions, carbon dioxide with water and the ionization of carbonic acid,



is affected by both temperature and pressure. Increase in pressure increases the weight of gas dissolved and favors the formation of carbonic acid and hydrogen ions. For this reason carbonated beverages are kept under pressure. When the pressure in a bottle of carbonated beverage is released by removing the bottle-cap, the equilibrium is changed with the formation of more carbon dioxide gas as indicated by the effervescence. If the beverage is warm there is more effervescence than if cold because a higher temperature favors the decomposition of the carbonic acid, and because the gas is less soluble in warm than in cold water.

The Mass Law. — The influence of concentration upon the speed of reactions is quite definitely expressed in an important principle known as the **mass law**, which may be stated as follows: *Other factors remaining constant, the speed of a chemical reaction is proportional to the molar concentration of the reacting substances.* This law is well illustrated by the equilibria just studied:

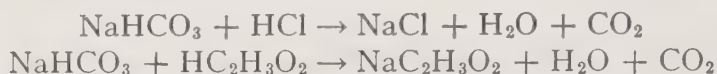


At a constant temperature and pressure, an equilibrium exists between all of the components of the reaction; the carbon dioxide and water are uniting to form carbonic acid at the same speed as the carbonic acid is being decomposed, and the carbonic acid is being ionized at the same speed as the ions are recombining to form molecules.

Any change in the concentration of one of the reactants will change the speed of one reaction, until a new equilibrium mixture is formed. Thus, addition of an acid (hydrogen ions) to the reaction mixture will increase the rate with which hydrogen ions combine with carbonate ions, and will favor the formation of carbon dioxide; the new equilibrium mixture will contain fewer car-

bonate ions and more carbon dioxide gas. On the other hand, addition of more carbon dioxide to the mixture will speed the reaction forming carbonic acid and thus result in more hydrogen ions in solution.

In the home we are often interested in the reverse of the reaction just studied — the formation of carbon dioxide from the action of an acid with baking soda. Would baking soda (NaHCO_3) react more readily with hydrochloric or with acetic acid? This question may be answered by an application of the mass law. The following equations are involved:

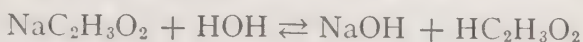


It is evident that these reactions have a tendency to go to completion because of the formation of carbon dioxide gas, which is a decomposition product of carbonic acid H_2CO_3 . Therefore, the reaction which furnished the greater number of hydrogen and carbonate ions would proceed most readily in a forward direction. Since NaHCO_3 is common to both reactions, the concentration of the carbonate ion is the same. However, it has been explained that the concentrations of hydrogen ion in hydrochloric acid and in acetic acid are not alike. Hydrochloric, a strong acid, furnishes a much greater concentration of hydrogen ion than acetic acid. Therefore, the formation of carbonic acid, and the resulting effervescence of carbon dioxide, would be more rapid from the reaction of hydrochloric acid with baking soda than from the reaction of acetic acid with baking soda. In these reactions, it is the concentration of hydrogen ion which determines the speed and the direction of the reaction.

Further applications of the mass law to reversible reactions and equilibrium mixtures will be given in the study of hydrogen ion concentration and buffer action (Chapter XV).

Hydrolysis. — Water is so slightly ionized that in most cases it does not enter into double decomposition reactions. However there is a type of double decomposition reaction, known as **hydrolysis**, in which a substance reacts with the hydrogen and hy-

droxyl ions of water. The substances which are known to react in this way are certain salts and, in the presence of a catalytic agent, certain non-electrolytes such as sugars and fats. The hydrolysis of sugars and fats will be discussed in later chapters. The hydrolysis of a salt is illustrated by the equation:



This reaction has a little tendency to go to completion because of the formation of a slightly ionized acid (acetic). Since sodium hydroxide, a strong base, is formed, the water solution of sodium acetate has an excess of hydroxyl ions and shows a basic reaction. It may be noted that the reaction between a salt and the ions of water is the reverse of neutralization. The reaction is indicated as being reversible; in fact the molecules of water are less ionized than those of acetic acid, hence the neutralization reaction is more nearly complete than the hydrolysis. However, the solution is distinctly basic, which indicates that hydroxyl ions of sodium hydroxide predominate in the solution, while the hydrogen is held in undissociated molecules of acetic acid. In order that the reaction of a salt with water may tend to go to completion, some slightly ionized substance must be formed. It follows that salts differ in this property of reacting with water in hydrolysis. For example, sodium carbonate, a salt of a weak acid, hydrolyzes in water solution, while sodium chloride, a salt of a strong base and a strong acid, does not undergo hydrolysis.

To summarize: in hydrolysis, a salt reacts with water to form an acid and a base. This type of reaction does not go to completion but will react sufficiently to give a test with litmus if either the acid or base formed is weak. If both acid and base are weak, the reaction goes to completion, but unless the relative ionization of both are known one cannot determine by inspection how the solution will react to litmus.

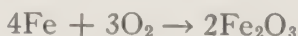
Hydrolysis of salts is often of value in the home. Salts which give a basic reaction are effective in the laundry and in cleaning. Such salts are washing soda, Na_2CO_3 , borax, $\text{Na}_2\text{B}_4\text{O}_7$, and sodium phosphate, Na_3PO_4 . Solutions of zinc chloride, ZnCl_2 , and aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3$, hydrolyze to give an acid reaction. Be-

cause of hydrolysis, zinc chloride may be used as a disinfectant and aluminium sulphate takes the place of an acid in certain baking-powders.

PREPARATION OF COMPOUNDS

Most of the elements occur naturally in a combined form, but we so often need compounds which are not found in nature that we have had to devise ways to make them ourselves. There are abundant deposits containing sodium chloride (common salt), but we must manufacture our own baking soda (sodium acid carbonate) and our own washing soda (sodium carbonate). Calcium carbonate in the form of limestone is plentiful, but other compounds of calcium, such as calcium oxide and bleaching-powder, must be manufactured. It is necessary for chemists to devise practicable methods for the preparation of these various compounds, using the least expensive substances as they occur in nature and the simplest and most efficient methods possible. An outline of the general methods used for commercial preparations will make it possible for the student to devise methods for preparing compounds needed in the laboratory.

Preparation of Oxides. — 1. *Direct Union of the Metal with Oxygen.* At high temperatures oxygen combines with nearly all metals. A typical equation follows:



2. *Decomposition of the Hydroxide.* Most hydroxides yield an oxide and water when heated. The following reaction illustrates the method:



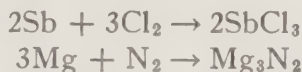
3. *Decomposition of Salts.* Carbonates of metals decompose when heated, giving up carbon dioxide gas. Lime, CaO , is thus prepared from limestone as shown by the equation:



Nitrates of metals (except those of sodium and potassium) decompose to form oxides. The following equation is typical:



Preparation of Salts. — 1. *Direct Union of Elements.* Binary compounds such as chlorides, sulphides, and nitrides may be prepared by direct union of elements. The following equations illustrate the reaction:



2. *Reaction of a Metal with Dilute Acid.* All metals preceding hydrogen in the electrochemical series react with dilute acids to give a salt of the metal. It is easy to prepare zinc chloride, zinc sulphate, magnesium chloride, and many other salts by this method. It is evident, however, that the method cannot be used for the preparation of salts of those metals occurring below hydrogen in the electrochemical series.

3. *Reaction of a Base with an Acid.* This method is satisfactory for the preparation of all salts. It is a neutralization type of reaction which continues to completion because of the formation of water. The reaction is illustrated by the following equation:

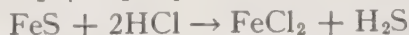
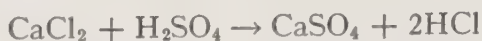


4. *Reaction of an Oxide of a Metal with an Acid.* This method is satisfactory also for the preparation of all salts. A typical reaction follows:



5. *Reaction of a Salt with an Acid.* This method is not applicable to the preparation of all salts. It is a double decomposition reaction and must go to completion through the formation of a precipitate or of a volatile acid. This type of reaction is used commercially in the preparation of several acids, for example nitric, hydrochloric, and hydrosulphuric. The salts are obtained

as by-products of the reaction. Typical reactions are the following:



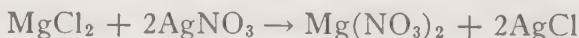
6. *Reaction of a Salt with a Salt.* When the two soluble salts — barium chloride and sodium sulphate — are mixed, immediately a white insoluble salt, barium sulphate, is formed making the reaction go to completion. The following reaction occurs:



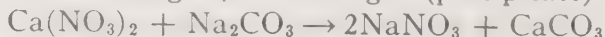
The reaction, in ionic form, is:



The precipitated barium sulphate may be separated by filtration from the sodium chloride in solution; crystals of sodium chloride may be obtained by evaporation of the filtrate. A successful double decomposition reaction of this type requires that the original reactants be two soluble salts and the products of the reaction must include one insoluble and one soluble salt. In order to devise a reaction of a salt with a salt, it will be necessary to determine the solubility of compounds (Appendix, Section 6). Typical illustrations of the use of this method for the preparation of salts are shown in the following equations:



The reaction, in ionic form, is:



The reaction, in ionic form, is:



QUESTIONS AND PROBLEMS

1. Using the electrochemical series, answer the following questions:
 - (a) Which metals react and which metals do not react with dilute acids? What is the type of reaction?
 - (b) Which are the most reactive metals? Which are the least reactive?
 - (c) Which metals give electrons most readily? Which metals give electrons least readily?
 - (d) Which metals give electrons to hydrogen ions? Which metals do not give electrons to hydrogen ions?
 - (e) Name some metals that will displace the following metals from their salts: Cu from CuSO_4 ; Fe from FeCl_3 ; Ag from AgNO_3 ; Ni from NiSO_4 .
 - (f) Will Cu displace Zn from ZnSO_4 ? Explain your answer.
2. Use the electrochemical series to determine which of the following reactions will be successful and which will not take place; write the balanced equation (and also the ionic form) for each successful reaction.
 - (a) zinc with copper nitrate
 - (b) copper with hydrochloric acid
 - (c) zinc with sulphurous acid
 - (d) iron with mercuric nitrate
 - (e) aluminium with sulphuric acid
 - (f) aluminium chloride with copper
 - (g) mercury with copper chloride
 - (h) silver with hydrochloric acid
 - (i) aluminium with acetic acid.
3. Write names and formulas for four gases that may be formed to make double decomposition reactions go to completion.
4. The following reactions go to completion because a gas is formed. Write them as balanced equations (and also in ionic form), and indicate the substance which is a gas:
 - (a) calcium carbonate + nitric acid \rightarrow
 - (b) potassium chloride + sulphuric acid \rightarrow
 - (c) aluminium sulphide + hydrochloric acid \rightarrow
 - (d) ammonium chloride + calcium hydroxide \rightarrow
5. Write names and formulas for four insoluble compounds that may be formed to make double decomposition reactions go to completion.
6. The following reactions go to completion because a precipitate is formed. Write them as balanced equations (and also in ionic form) and indicate the substance which is insoluble:
 - (a) aluminium sulphate + barium chloride \rightarrow
 - (b) calcium nitrate + sodium carbonate \rightarrow
 - (c) silver nitrate + ? \rightarrow silver chloride + ?
 - (d) ferrous chloride + ? \rightarrow ferrous sulphide + ?

7. Write five neutralization reactions as balanced equations (and in ionic form) and tell why they go to completion.
8. A few of the following reactions will not go to completion. Write the successful reactions as balanced equations (and in the ionic form) and tell why the reactions go to completion: (See Appendix, Section 6).
- | | |
|---|--|
| $\text{Ba}(\text{NO}_3)_2 + \text{Ag}_2\text{SO}_4 \rightarrow$ | $\text{Zn}(\text{OH})_2 + \text{H}_2\text{SO}_4 \rightarrow$ |
| $\text{NaNO}_3 + \text{MgCl}_2 \rightarrow$ | $\text{CaCl}_2 + \text{AgNO}_3 \rightarrow$ |
| $\text{ZnS} + \text{H}_2\text{SO}_4 \rightarrow$ | $(\text{NH}_4)_2\text{CO}_3 + \text{H}_3\text{PO}_4 \rightarrow$ |
| $\text{CaCO}_3 + \text{HCl} \rightarrow$ | $\text{KCl} + \text{NaNO}_3 \rightarrow$ |
| $\text{ZnCl}_2 + (\text{NH}_4)_2\text{SO}_4 \rightarrow$ | $\text{NaOH} + \text{H}_2\text{C}_2\text{O}_4 \rightarrow$ |
9. Write equations to show the hydrolysis of washing soda, borax, and sodium phosphate. What is the reaction of each solution to litmus? Explain a household application of the hydrolysis of salts.
10. What type of salts undergo hydrolysis? If hydrolysis occurs with the following salts, write equations for the reaction (omit those for which no reaction occurs):
- | | |
|----------------------|-------------------------|
| (a) ferric nitrate | (e) potassium sulphate |
| (b) sodium carbonate | (f) ammonium sulphide |
| (c) sodium chloride | (g) aluminium sulphate |
| (d) zinc chloride | (h) potassium phosphate |
11. The following reactions include displacement, double decomposition, hydrolysis, acid and basic anhydride with water. Write as balanced equations, classify the reactions, tell why they go to completion (if double decomposition):
- (a) ammonium sulphate + barium nitrate
 - (b) zinc + mercury nitrate
 - (c) sulphur trioxide (SO_3) + water
 - (d) ferrous sulphide + sulphuric acid
 - (e) ammonium carbonate + water
 - (f) calcium oxide + water
 - (g) zinc sulphate + water
 - (h) sulphur dioxide + water
12. Write equations to illustrate three methods for the preparation of aluminium oxide.
13. Write equations to show five methods for the preparation of zinc sulphate.
14. Write equations for reactions that could be used for the following preparations:
- (a) zinc nitrate by reaction of an oxide with an acid
 - (b) magnesium nitrate by reaction of a salt with an acid
 - (c) potassium sulphate by reaction of a base with an acid
 - (d) magnesium chloride by reaction of a metal with an acid
 - (e) ferric chloride by direct union of elements
 - (f) sodium sulphate from sodium chloride with ?

- (g) ferrous sulphide from ferrous chloride with ?
- (h) zinc chloride from zinc sulphate with ?
- (i) calcium chloride from calcium hydroxide with ?

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CHAPTER XV

HYDROGEN ION CONCENTRATION

Importance. — We have learned that the intensity of the properties of an acid depends upon the concentration of hydrogen ion (H^+), existing in the solution as hydronium ion, H_3O^+ . Just as the saltiness of a solution depends on the concentration of salt in it, the sourness of a solution depends on the concentration of hydrogen ions.

It is important, however, to have in mind that it is only the ionized hydrogen that can affect the taste of a solution, and because the effective ionization of acids differ, the sourness of acid solutions of the same normality may differ considerably; for example, hydrochloric acid and acetic acids in one-normal solution each contain one gram of combined hydrogen in the liter, but because of a difference in ionization the solutions do not taste equally sour. However, one gram-molecular weight of sodium hydroxide would be required to neutralize the liter of either the one-normal hydrochloric or the one-normal acetic acid. This is known as **titratable acidity**. The hydrochloric acid is a strong acid and completely ionized. Because of interionic attraction, the effective ionization in a one-normal solution is 79.6 per cent. Compared to this, acetic acid, a weak acid, contains in one-normal solution only 0.37 per cent of ions. Therefore, one-normal hydrochloric acid would have to be diluted 250 times, to 0.004 normal, in order to have the same hydrogen ion concentration or sourness as the one-normal acetic acid.

Because the sour taste of vinegar is caused by the acid or the hydrogen ions in solution, we can realize that a "synthetic vinegar" might be made by flavoring any inexpensive inorganic acid, such as hydrochloric acid. Sometimes this was done before the Food and Drugs Act (1903) was passed, but the adulteration can be detected because the acid used as an adulterant has a different

percentage of ionization from the acids normally present in vinegar. Cider vinegar contains between 4 and 5 per cent of acetic acid in solution, making it approximately a two-thirds or 0.67-normal solution. In this concentration the acetic acid is 0.47 per cent ionized, making the hydrogen ion concentration not more than 0.003-normal. Hydrochloric acid is a strong electrolyte, or in other words is 100 per cent ionized; therefore a solution of this acid with the same hydrogen ion concentration (or sourness) as vinegar would be only 0.003-normal. It is a simple matter for a chemist to distinguish by titration between a 0.67-normal solution and a 0.003-normal solution and thus detect the adulteration.

Since not only taste but all the acid properties depend on the hydrogen ions in solution, the strong or highly ionized hydrochloric acid exhibits all these properties much more than the weak or slightly ionized acetic acid with the same titratable acidity.

As we have learned, hydrochloric acid reacts more vigorously with baking soda and metals than acetic acid does, and it will change the color of indicators that acetic acid will not affect. The acids present in foods, in the body, in the soil, and elsewhere play an important part in the various phases of life. Hence it is necessary to study acids with special reference to one of their important properties, hydrogen ion concentration.

Review of Mathematics. — Before studying the methods used to calculate and to express the hydrogen ion concentration of solutions, it is well to review the methods of designating very large or small quantities in mathematics. In science it is often necessary to work with these quantities. We have learned that a gram-molecular weight of any pure substance contains 6.06×10^{23} molecules, and that the weight of one atom or molecule in grams is an inconceivably small number. In this case the number, 606,000,000,000,000,000,000, is expressed as above by placing the decimal after the first digit and multiplying this number by 10 with the proper exponent. In a similar way, 1,400 is expressed as 1.4×10^3 , and 2,000,000 is written 2×10^6 . Since the exponent of 10 indicates the number of digits, it is the most significant

number in the expression. When it is necessary to express a fractional quantity, negative exponents are used. Thus the fraction $1/100$ is written 10^{-2} or $1/10^2$, and the fraction $42/10,000$ is written 4.2×10^{-3} or $4.2 \times 1/10^3$. In order to multiply two numbers in this form the exponents are added. Division is accomplished by subtracting exponents. Thus, $10^6 \times 10^4 = 10^{10}$ and $10^6 \times 10^{-4} = 10^2$, while $10^6 \div 10^4 = 10^2$. Problems illustrating the use of these expressions will be found at the close of this chapter.

Relation of the Mass Law to Hydrogen Ion Concentration. —

Experiments have shown that even pure water ionizes to a small extent, coming to an equilibrium when the molar concentrations of the H^+ and OH^- ions are each 10^{-7} . At this point the ions are combining at the same rate as the molecules of water are ionizing or separating. The equation for the reaction is:



The mass law (Chapter XIV) states that the rate of any chemical reaction is proportional to the molar concentration of the reacting substances. Since water molecules are present in such a large proportion compared to the H^+ and OH^- ions, they may be neglected in any calculations that apply the mass law to the equation given. Thus only the H^+ ions and the OH^- ions need be considered.

Since the molar concentrations of H^+ and OH^- ions in pure water are each 10^{-7} , the product of the molar concentration of the reacting substances is 10^{-14} . This is usually expressed as follows:

$$C_{H^+} \times C_{OH^-} = 10^{-14}$$

In this expression, C_{H^+} and C_{OH^-} represent the molar concentrations of these ions. It will be noted that if C_{H^+} in solution is increased by adding an acid, C_{OH^-} is decreased by the ions uniting to form water until the product is 10^{-14} . Conversely, when C_{OH^-} is increased by adding a base, C_{H^+} must decrease until the product of the two is again 10^{-14} . In other words, when the concentration of either ion becomes greater, the concentration of the other ion becomes less, because there is more opportunity for the ions to

meet in the solution and combine. Equilibrium occurs only when the ions meet and combine at the same rate as the water molecules separate, that is when $C_{\text{H}^+} \times C_{\text{OH}^-} = 10^{-14}$. These concentrations may seem too small to be of interest until we realize that the acid of lemon juice has a hydrogen ion concentration of about 10^{-2} , while ammonia water may have a hydroxyl ion concentration of about 10^{-2} . Most of the acids and bases that we use in the home have hydrogen and hydroxyl ion concentrations nearer neutrality than these. This formula has many applications in the study of the strength of acidic and basic solutions, and it is the basis of an interesting and convenient method of expressing acidity. A few examples will illustrate this use.

Experiments show that a 0.001-molar sodium hydroxide solution is completely ionized. In other words, the molar concentration of the hydroxyl ions in the solution (C_{OH^-}) is 10^{-3} . From the formula just given it is possible to calculate the hydrogen ion concentration of this solution.

$$\begin{aligned} C_{\text{H}^+} \times C_{\text{OH}^-} &= 10^{-14} \\ C_{\text{H}^+} \times 10^{-3} &= 10^{-14} \\ C_{\text{H}^+} &= 10^{-14}/10^{-3} = 10^{-11} \end{aligned}$$

In another case, we might be told that the hydrogen ion concentration of a solution is 10^{-9} . Since this is less than 10^{-7} we know that the hydroxyl ions are present in higher concentration than the hydrogen ions and thus that the solution is basic. The exact hydroxyl ion concentration may be calculated from the formula:

$$\begin{aligned} C_{\text{H}^+} \times C_{\text{OH}^-} &= 10^{-14} \\ 10^{-9} \times C_{\text{OH}^-} &= 10^{-14} \\ C_{\text{OH}^-} &= 10^{-14}/10^{-9} = 10^{-5} \end{aligned}$$

Again, the strong ammonia water (NH_4OH), for which the hydroxyl ion concentration was given as 10^{-2} , may be described as having a hydrogen ion concentration of 10^{-12} . It is evident that *whenever C_{OH^-} is known for a solution, C_{H^+} may be calculated; and that when C_{H^+} is known, it is possible to calculate C_{OH^-}*

The *pH* Method of Expressing Hydrogen and Hydroxyl Ion Concentration. — That the low concentrations of hydrogen and hydroxyl ions are difficult to express, either in the form of decimals or as an exponent of 10, has been suggested in the foregoing paragraph. A simpler and quicker method of stating hydrogen ion concentration consists in using just the exponent of 10 and omitting the negative sign. This method, in common use in all textbooks, is known as the ***pH* value**, meaning hydrogen ion potential. Thus a hydrochloric acid solution, 0.001-molar and having a hydrogen ion concentration of 10^{-3} , has a *pH* value of 3. A 0.001-molar sodium hydroxide solution, having a hydrogen ion concentration of 10^{-11} , has a *pH* value of 11. Since the hydrogen ion concentration of foods, blood, urine, dyes, soils, and countless other substances is so important and is commonly expressed as *pH* value, it is necessary to become familiar with this system.

Note that the solutions that contain the higher concentration of hydrogen ions have a lower *pH* value; for example, when the hydrogen ion concentration of a solution is 0.01- (or 10^{-2}) molar, the solution has a *pH* of 2; when the hydrogen ion concentration of a solution is 0.00001 (or 10^{-5}) molar, the solution has a *pH* value of 5. The solution with a *pH* of 2 has 1,000 times the hydrogen ion concentration of the solution with a *pH* of 5. Any solution with a *pH* value less than 7 has a hydrogen ion concentration which is greater than the hydroxyl ion concentration, and it follows that the solution is acidic. If the *pH* value of a solution is greater than 7, the hydroxyl ion concentration is greater than the hydrogen ion concentration, and the solution is basic.

We must think of the *pH* system of expressing the hydrogen ion concentration as an arbitrary method of stating the intensity of acid or basic properties of a solution. The *pH* value may vary from 0 to 14. The hydrogen ion concentration of a solution with a *pH* value of 0 is 10^0 or 1-molar, while the hydrogen ion concentration of a solution with a *pH* of 14 is 10^{-14} molar. *As the pH value increases from 0 to 7, the intensity of acid action decreases until the solution is neutral. As the pH value increases from 7 to 14, the intensity of the basic properties increases.* When the hydrogen or hydroxyl ion concentration is greater than one-molar, the

pH system is not practical and other methods are usually used. When the hydrogen ion concentration is not an even power of 10, for example 4×10^{-3} , it is still possible to express it in terms of *pH* value, but in order to do this it is necessary to understand the use of logarithmic tables.

Methods of Determining the Hydrogen Ion Concentration or *pH* Value of Solutions. — Since hydrogen ions have an electric charge, many electrical methods have been devised for determining *pH* value, but they are too complicated and expensive for use in elementary work. In the laboratory experiments, we have noted that many dyes change color when added to acidic or basic solutions. We learned also that while the indicator, litmus, changes in color when the solution is neutral (*pH* = 7), methyl orange does not change until it is quite acid (*pH* about 4.4), and phenolphthalein begins to show a red color when the solution is slightly basic (*pH* about 8). Other indicators or dyes are known which change color at every *pH* value from 0 to 14. This makes it possible to determine the hydrogen ion concentration of solutions by colorimetric methods.

Indicators do not change in color suddenly. When an acid or base is added, one color gradually develops as the other color fades away. For example, during the titration of a weak acid solution with methyl orange as an indicator, the color gradually changes from red to yellow and the exact end-point is difficult to determine. In other words, several drops of base may be added in excess before one realizes that the yellow color has appeared. It is certain that this color change will occur when the solution is at a *pH* of 3.2 to 4.4, and this is a help in determining *pH* values colorimetrically. If methyl orange gives a clear yellow color in a solution, we know that the solution has a *pH* value that is greater than 4.4. If it is a clear red color, we know that the solution has a *pH* value less than 3.2. If, however, methyl orange gives a red-orange color to a solution, we know the *pH* value is between 3.2 and 4.4, and by observing the exact shade of color we can tell whether it is more red (nearer a *pH* of 3.2) or more yellow (nearer a *pH* of 4.4). Some of the useful indicators and the color changes

are given in Table XIII. A longer list may be found in the appendix.

TABLE XIII

pH AND COLOR CHANGE OF INDICATORS

<i>Indicator</i>	<i>pH range</i>	<i>Color change</i>
Thymol blue (acidic range)	1.2 — 2.8	red to yellow
Thymol blue (basic range)	8.0 — 9.6	yellow to blue
Brom phenol blue	3.0 — 4.6	yellow to purple
Methyl red	4.2 — 6.3	red to yellow
Brom thymol blue	6.0 — 7.6	yellow to blue
Phenol red	6.8 — 8.4	yellow to red

The change in color of the indicators may be made useful in several ways to determine the *pH* value of solutions. Charts have been made that show the exact shades of several indicators for every 0.2 *pH* in the range of the color change. When we wish to determine the *pH* value of a solution, we add definite amounts of indicator to 10-c.c. portions of the solution until we find an indicator that has neither its acid nor its base color, but a combination of both. We may then compare this color with those on the chart for this indicator and thus determine the *pH* closely. It is difficult to paint colors that are exact duplicates of solution colors, and several methods have been devised to prepare more accurate standards with which to compare the colors of indicators in solution. One method makes use of colored glass slides that fit into a comparator box with which solution colors may be more easily compared than with those on paper. Another method makes use of a series of solutions that have every *pH* value desired so that indicators may be added to these to give the accurate color at each *pH* value.

Buffer Action. — In solutions of weak acids or bases with an excess of their salts, there is a tendency to maintain a constant *pH* value; illustrations of such mixtures are acetic acid with sodium acetate, or ammonium hydroxide with ammonium chloride. These mixtures are called **buffers**. In such solutions, the amount of acid or of base that must be added to cause a definite change in *pH* of the

solution is greater than when the acid or base is added to simple water solutions.

The action of buffers can be understood by an application of the mass law (Chapter XIV); for example, in a mixture of acetic acid with sodium acetate we have the equilibrium equation for the weak acid:



The addition of sodium acetate, a salt which is entirely in the form of ions, increases the concentration of the acetate ion. Thus, the reaction is reversed, forming a large reserve of acetic acid molecules as well as acetate ions, with only a comparatively low concentration of hydrogen ions. If hydrochloric or any other acid is added to this buffer mixture, the reserve of acetate ions will tend to combine with the hydrogen ions of the added acid to form acetic acid molecules, and again remove most of the hydrogen ions from solution. As a result, the change in $p\text{H}$ will be less than expected. If sodium hydroxide or any base is added to the buffer mixture to neutralize the hydrogen ions by combining with them to form water, some of the reserve acetic acid molecules will be free to ionize, to furnish hydrogen ion, and so balance the loss caused by addition of sodium hydroxide. In other words, the change in $p\text{H}$ will be slight. Buffer mixtures are present in all plant and animal life and help to keep the $p\text{H}$ of liquids in such cells near neutrality.

Practical Applications of $p\text{H}$ Value and Buffer Action. — *Baking.* A solution with a high $p\text{H}$ value (basic reaction) tends to dissolve or to disintegrate protein. In a solution with a low $p\text{H}$ value, protein absorbs water and becomes tender but does not disintegrate. Since the texture of baked goods depends primarily on the condition of the gluten in the flour, it is easy to see that it is quite dependent on the $p\text{H}$ value of the baking mixture. In bakeries, where success depends on the production of a uniform product, the $p\text{H}$ determinations are made daily.

We have probably noted the effect of $p\text{H}$ value on light breads when we compare the coarse texture of a biscuit or gingerbread

made with an excess of baking soda with the fine texture of a biscuit made with baking powder.

Other Cookery. When an acid is added in stewing tough meats, hydration occurs and the meat becomes tender more quickly. Tomato juice is sometimes used in omelets to make them more tender. Baking soda may be added in cooking beans, because it helps to make them soft. Fruit juices of various kinds are used with gelatin, not only to give an acid taste, but also to make it hydrate more easily and become more tender. Commercial gelatin mixtures for quick desserts are made with the optimum pH value to give a tender solid gel. When gelatin is mixed with fruit juices of various acidities in the kitchen, the optimum pH value can only be approximated.

Fruit jelly consists of a mixture of fruit flavors, pectin, acid, and sugar. Since no two kinds of fruit and no two samples of fruit of the same kind are alike in flavor, pectin content, and acidity, it is difficult to duplicate conditions and thus to have uniform results. In commercial firms the pH value, pectin, and sugar content are definitely controlled. Research on jellies has shown that the best jelly contains 0.75 to 1.25 per cent pectin and 60 to 70 per cent sugar, and has a pH value near 3.4. A high acidity or low pH value is apt to give a stiff jelly or one that tends to water or "sweat." The acids in fruits are usually organic, such as tartaric, citric, or malic acids. They are always buffered with salts of these acids, which increases the pH value (lowers the acidity) and makes it difficult to change the pH value by the addition of either acid or base.

Bacteria are more easily killed by heat in a solution with a low pH value. As a result, canning of acid fruits and vegetables is easier and more successful than canning non-acid vegetables and meats.

Textiles. We have learned that bases tend to disintegrate the textiles that are protein in composition, such as silk and wool. Since most soaps and washing-powders are basic in reaction, it is important to know how strongly basic they are (their pH value), before washing silk or woolen goods with them. This can easily be determined colorimetrically.

Dyes. Some dyes cling to fibers more readily in a solution with a low pH value; others dye better in a solution with a high pH value. In industries the pH value is carefully controlled. In home dyeing it is necessary to follow the directions given on the package for any particular dye.

Nutrition. The constancy of the pH value of the body fluids is surprising. Many experiments have shown that in normal blood it is very close to 7.4, and that a pH value outside the range of 7.3 to 7.5 is a sign of disease, while a pH of 7.0 or lower causes coma and a pH of 7.8 or higher causes tetany.

The foods we eat, when digested and absorbed, have a definite effect on the pH value of the blood. In choosing a diet it is important to take this fact into consideration. The pH value of a food when digested is easily determined, since it is only necessary to find the pH of a water solution of the ash left when the food is burned. Experiments of this type have shown that most fruits and vegetables have a basic ash, while meat and cereals have an acid ash. Studies made of the average American diet seem to indicate that most people eat too little of the foods which have a basic ash.

One would think that the formation of lactic acid and of carbonic acid from muscular action and the absorption of excess acid or basic foods after a meal or the secretion of hydrochloric acid into the stomach during digestion might have a considerable effect on the pH value of the blood. Although experiments have shown that there actually is a decrease in pH value of 0.01 to 0.031 after strenuous exercise and an increase of a similar amount after meals, the effect is small because of the buffer action of the salts in the blood. Just as sodium acetate prevents the ionization of acetic acid in a solution, sodium or potassium carbonate or phosphate prevents the ionization of carbonic and phosphoric acids. Even the proteins and hemoglobin in the blood act as buffers, sometimes as a weak acid (H protein) and sometimes as the salt of that acid (Na protein).

An important application of our knowledge of buffer action has recently been made in the adaptation of cow's milk to resemble the human mother's milk for babies. Because cow's milk has a

slightly lower pH value than breast milk, physicians once recommended the addition of lime-water or other mild bases to make it suitable for babies. Recently research workers have found that the buffer value of cow's milk is so high that it may almost neutralize the acid in the baby's stomach. The resulting high pH value may cause the calcium in the milk to be precipitated and thus prevent it from being absorbed into the blood. This may bring about a deficiency of calcium and be the cause of the disease rickets. Physicians now add acids to milk instead of bases to keep the pH value of the stomach low enough to make possible the absorption of the calcium.

The applications of hydrogen ion concentration control in industry are numberless. In the manufacture of paper, rayon, linen, cotton, leather, gelatin, flour, and countless other substances, accurate pH control is essential to ensure a uniform and standard product.

QUESTIONS AND PROBLEMS

- Express exponentially: 1,000; 800; 540,000,000,000; 0.00001.
- Change to integral numbers or decimals: 10^3 ; 10^{-7} ; 6×10^{23} ; 4×10^{-2} .
- Multiply: $10^7 \times 10^6$; $10^{-8} \times 10^{-3}$; $10^{-4} \times 10^3$.
- Divide: 10^8 by 10^4 ; 10^{-5} by 10^{-2} .
- Which number is larger, 10^{-10} or 10^{-6} ? How many times as large?
- Determine the hydrogen ion concentration of the following and tell whether each solution would test acidic, basic, or neutral to litmus:
 - a solution with a pH of 4
 - a solution with a pH of 8
 - a solution with a pH of 2
 - a solution with a pH of 7
- Determine the pH value of the following:
 - a solution with a hydrogen ion concentration of 0.01
 - a solution with a hydrogen ion concentration of 10^{-4}
 - a solution with a hydroxyl ion concentration of 0.001
 - a solution with a hydroxyl ion concentration of 10^{-5}
- The indicator brom thymol blue is blue in basic solution and yellow in acid solution. If when added to a solution it turns green, what do we know of the pH value of the solution?
- Which is more acid, a solution with a pH of 5 or one with a pH of 6? How many times as acid?
- Which is more basic, a solution with a pH of 13 or one with a pH of 14? How many times as basic?

11. Determine the hydrogen ion concentration of the following solutions:
 - (a) 0.01N HCl (completely ionized)
 - (b) 0.05N $\text{HC}_2\text{H}_3\text{O}_2$ (2 per cent ionized)
 - (c) 0.06N H_3PO_4 ($16\frac{2}{3}$ per cent ionized)
 - (d) 0.05N NH_4OH (2 per cent ionized)
12. Explain the effect of adding sodium citrate to lemonade (citric acid solution).

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CHAPTER XVI

CARBON. OXIDES OF CARBON. ACIDS OF CARBON

WITHOUT doubt the element carbon deserves a place near the head of a list of important elements. In the impure form of soft and hard coal, carbon occurs in deposits throughout the earth's surface. Compounds of carbon are most abundant; carbon dioxide is an important constituent of the atmosphere, and other carbon compounds are present in every type of living matter. Wood, paper, textiles, foods, and fuels are carbon compounds. Because of the variety, complexity, and importance of carbon compounds, a consistent study of them (organic chemistry) is one of the separate branches of advanced chemistry. Only the element, its oxides, and a few other compounds will be described at present. A further study of other carbon compounds is given in Chapter XXIX.

Destructive Distillation. — When organic matter, such as wood, coal, or bones, is heated in a retort from which air is excluded, decomposition takes place. If the heat is continued until no further change occurs, there is formed a solid residue of carbon (often mixed with impurities). A very pure form of carbon is obtained when sugar is heated to decomposition. Similar cases of partial destructive distillation take place when food is heated to decomposition (burned) in the oven.

The destructive distillation of wood in earthen ovens to form charcoal has been practised for many years. As the wood is heated, gases are evolved, part of which may be condensed to a liquid. From this liquid, wood alcohol, acetic acid, and other important compounds may be separated and used for industrial purposes. The liquids may be of greater value than the charcoal residue.

When coal undergoes destructive distillation, the carbon residue

is coke, a clean, slow-burning fuel. Coke is useful in many industrial processes, such as the separation of metals from their oxides. Part of the gas evolved from coal is liquefied to form coal-tar. This contains many complex organic compounds from which synthetic drugs, perfumes, and flavorings are made. The remainder of the gas from the destructive distillation of coal is treated to remove ammonia and is used as a fuel gas, known as "coal gas," for the home and for industrial use.

Destructive distillation of bones forms a residue called bone-black. In sugar refineries, bone-black is used as a filtering medium to remove the brown color and the impurities from sugar syrups.

The incomplete combustion of kerosene and fuel oils causes the formation of a fine soft powdered carbon known as lampblack. It is familiar as the black "soot" that forms on the bottom of kettles over a wood or coal fire. Lampblack is produced commercially for use as a pigment in printers' ink, paints, polishes, and automobile tires. The incomplete combustion of natural gas also produces a form of amorphous carbon, known as carbon black, which is useful as a pigment.

Allotropic Forms of Carbon. — The kinds of carbon just mentioned are called amorphous (without form) in contrast to the crystalline forms of carbon, the diamond and graphite. By showing that the different forms of carbon oxidize to form carbon dioxide, chemists have proved that the diamond, graphite, and the residues obtained from destructive distillation of organic matter are all the same element carbon. The crystalline and the amorphous carbon, which together are called the allotropic forms of carbon, do not have the same physical properties or energy content. Several other elements which will be studied later occur in two or more **allotropic forms**, and the term carries the same meaning, that is, two or more forms of an element, each with a different set of physical properties and a different energy content.

The X-ray diffraction patterns (Chapter XII) of diamond and graphite indicate that the arrangement of atoms in the molecule is different in the allotropic forms of the element. These patterns show that the carbon atoms of the diamond are arranged in a

series of hexagons (Fig. 26) in which each atom is equidistant from four other atoms. In graphite, the hexagons of carbon atoms are arranged in layers in which the distance between the layers is



FIG. 26. Arrangement of Atoms in Diamond

much greater than the distance between the atoms in any layer (Fig. 27). This allows the layers of atoms to slip over each other, making graphite a good lubricant. In true amorphous substances, all atoms are arranged in a haphazard manner and thus they show no crystalline properties.

The crystalline forms of carbon may be made from amorphous carbon. Very small diamonds have been made by dissolving carbon in molten iron and quickly cooling the mass. It seems that the pressure of the outside solidified iron on the molten mass inside produces crystalline carbon in much the same way as it is thought that diamonds have been made in the earth. Diamonds are the hardest crystals known. They show their brilliance only when polished and cut.

Graphite is found in nature and may be made by heating carbon to a high temperature by means of the electric arc. Graphite is composed of tiny, grayish leaflets which slip and slide over each other in such a way as to make the substance useful as a lubricant and in "lead"-pencils. Graphite conducts electricity and so has many uses in batteries and electric furnaces.

Carbon Monoxide. — When carbon or its compounds burn in a limited supply of oxygen, carbon monoxide gas, CO , is formed. Recently, this gas has become all too familiar through the many deaths caused by its presence in the exhaust gas of automobiles, in coal gas, and in fumes from a coal stove or gas heater. Carbon monoxide is very poisonous. Inhalation for a few hours of air

containing 0.1 per cent of carbon monoxide may result in headache and nausea. Physiologically, the carbon monoxide combines with the hemoglobin of the blood, leaving none free to carry the oxygen to the tissues. Thus the gas has the same effect as asphyxi-

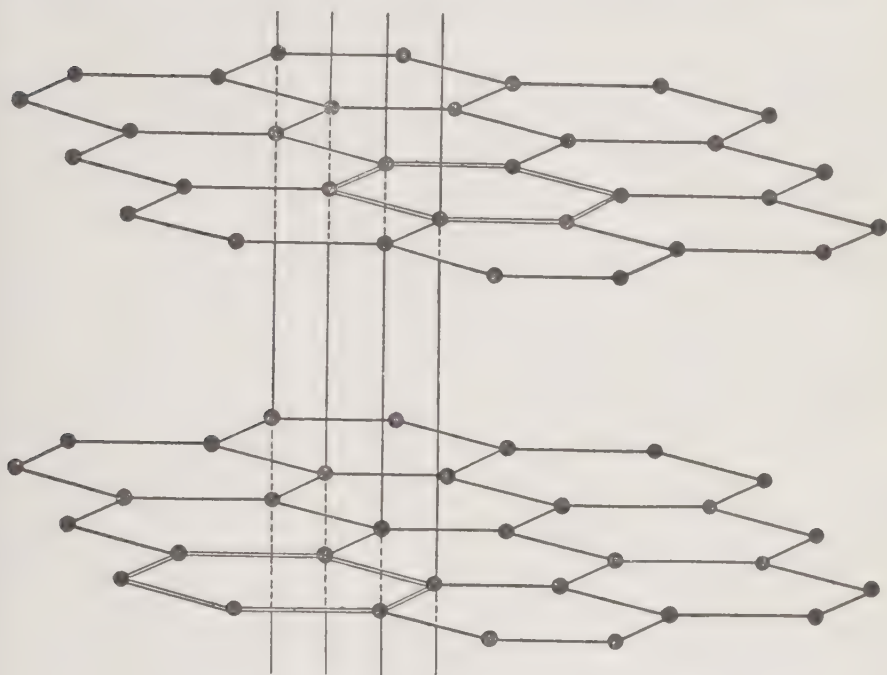


FIG. 27. Crystal Lattice Structure of Graphite

ation. It is especially dangerous because it is odorless and colorless and gives no warning of its presence.

Carbon monoxide burns readily with a hot bluish flame, and forms carbon dioxide, as shown in the equation:



It is an important constituent of coal gas and of water gas. The preparation of water gas, by passing steam over hot coke, has been mentioned (Chapter VI). Two combustible gases, hydrogen and carbon monoxide, are formed both of which burn with a hot flame.

Carbon Dioxide. — Carbon dioxide is familiar as the gas that forms the bubbles or foam in carbonated beverages, ice cream soda, and in a mixture of baking soda and acid. In frozen form, carbon dioxide is familiar as "Dry Ice." Carbon dioxide occurs in some underground deposits and in some spring waters.

Preparation. — 1. *Burning Carbon in Oxygen.* The equation for the reaction is: $C + O_2 \rightarrow CO_2$

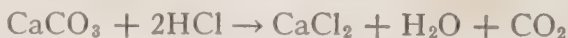
2. *Heating Certain Carbonates.* Perhaps the most abundant carbonate is limestone or calcium carbonate, $CaCO_3$. When calcium carbonate is heated for the production of lime, CaO , carbon dioxide also is formed, as shown by the equation:



3. *Action of Acid on a Carbonate.* When carbon dioxide is desired in baking, it is obtained by the reaction of baking soda or sodium acid carbonate, $NaHCO_3$ with sour milk (lactic acid), or possibly with baking soda and acetic acid as shown by the equation:



Carbon dioxide is obtained conveniently in the laboratory by the reaction of limestone or marble chips (calcium carbonate) with an acid according to the reaction:



The ionic equation which shows this type of reaction is that of the hydrogen ion of an acid with the carbonate ion of the salt, as:



Properties. — Carbon dioxide is a colorless, odorless gas, soluble in water. It is so much heavier than air that it may be poured from one vessel to another. At room temperature, high pressure will cause the gas to be condensed to a liquid. Carbon dioxide freezes to a solid at $-56.7^\circ C$. Under one atmosphere of pressure and $-78.5^\circ C$., solid carbon dioxide sublimates (changes directly



Courtesy of Dry-Ice Corporation of America

PACKING MEAT WITH "DRY-ICE"

The use of dry-ice in packing perishable material is widespread; for example, in the packing of meats, fish, game, dairy products, vegetables, fruits, and flowers. Motor trucks and refrigerator cars are equipped with dry-ice.

to a gas). Frozen carbon dioxide is a rival of water ice for refrigeration. No liquid is formed when solid carbon dioxide evaporates, and its effectiveness as a refrigerant is shown by the estimate that one pound of frozen carbon dioxide is equivalent to from fifteen to twenty pounds of water ice. Moreover, in the preservation of meat, fish, or fruit, the gaseous carbon dioxide settles around the refrigerated food and delays bacterial decomposition.

An interesting application is made of the use of carbon dioxide as a food preservative in the storage of dry products such as nuts.

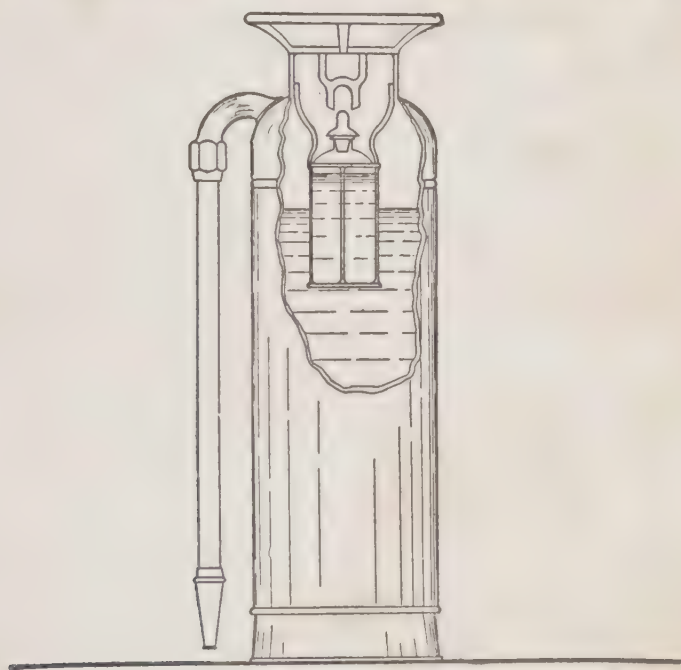


FIG. 28. Fire-Extinguisher

coffee, coconut, and evaporated milk in an atmosphere of carbon dioxide. It is used also to preserve cod liver oil and biological supplies. All these products are known to keep in better condition in the presence of carbon dioxide rather than oxygen.

Carbon dioxide has properties which make it useful as a fire extinguisher. It will not burn, and being a heavy gas it settles

around a flame and thus limits the amount of oxygen which is near the burning material. Certain types of fire extinguishers are constructed so that carbon dioxide is generated and poured on the flame (Fig. 28). This type of fire extinguisher is filled with a solution of sodium bicarbonate, and a bottle of sulphuric acid is suspended in the top. When the tank is inverted, the sulphuric acid flows into the sodium bicarbonate solution, and the following reaction occurs:



The mixture of carbon dioxide with sodium bicarbonate solution, which is evolved at the nozzle of the fire extinguisher, is efficient in preventing oxygen from reaching the burning material.

The fact that carbon dioxide is a colorless, odorless, and tasteless gas makes it valuable as a leavening agent in baking. Whether baking-powder, baking-soda, or yeast is used, the leavening of the dough is caused by the formation of carbon dioxide gas and its expansion when heated. The gas pushes up slowly through the dough and keeps it frothy until the heat can "set" or bake it.

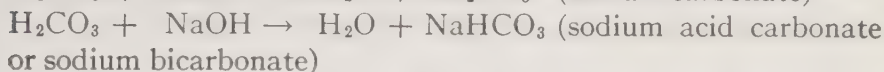
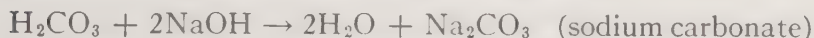
Carbon dioxide is an acid anhydride. Thus when the gas dissolves in water, it also reacts with the water, forming carbonic acid, according to the equation



Properties of Carbonic Acid. — Carbonic acid is a weak or slightly ionized acid. Since a saturated solution of carbon dioxide at 25° C. and 760 mm. pressure is only a 0.03-molar solution and the carbonic acid formed is but 0.33 per cent ionized, it is evident that the acidic properties are never important. At pressures higher than 760 mm., carbon dioxide is much more soluble in water, and the acid taste of carbonated beverages is partly owing to the fact that an excess of carbon dioxide is forced into the solution at high pressures.

Carbonic acid with any base may form two salts, the normal

salt and the acid salt. Thus with sodium hydroxide, the following reactions give the preparation of both salts:

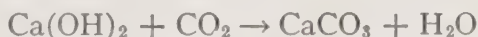


As has been mentioned, washing soda has the formula $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ and baking-soda is NaHCO_3 .

A Test for Carbonate and for Carbon Dioxide. — When an acid is added to a salt containing the carbonate ion, carbon dioxide gas is formed with bubbling or effervescence. The reaction has been studied in Chapters X and XIV, and in the preparation of carbon dioxide. In terms of ions, it is:



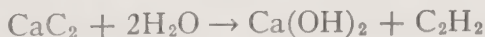
When the carbon dioxide, an acid anhydride, is allowed to bubble through the base, calcium hydroxide, the reaction is similar to the neutralization of a base with an acid. The following equation shows the reaction:



The appearance of the insoluble salt, calcium carbonate CaCO_3 , as a white precipitate constitutes a test for carbon dioxide.

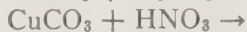
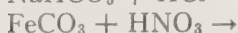
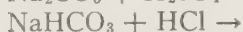
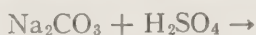
Carbides. — When carbon is heated in an electric furnace with certain oxides, it will form compounds called carbides. Two of these are of commercial importance. Silicon dioxide with coke forms silicon carbide SiC , which is called carborundum. It is almost as hard as a diamond and is resistant to acids. When powdered and molded with clay it is used for grinding and polishing metal surfaces.

Calcium oxide and coke form calcium carbide. This substance is of interest since it may be used for the preparation of acetylene, a fuel and illuminating gas. In the preparation of the gas, calcium carbide reacts with water according to the equation



QUESTIONS AND PROBLEMS

1. What is meant by the term **destructive distillation**? What are three products of the destructive distillation of soft coal; three products of the destructive distillation of wood?
2. Give meaning of the terms: bone-black, lampblack, allotropic forms, amorphous, graphite.
3. Give two examples of amorphous carbon and two examples of crystalline carbon. How may they all be shown to be the same element?
4. Why is a study of carbon monoxide important? Give its physical, chemical, and physiological properties.
5. What are the constituents of water gas? How is it made?
6. Write equations for three different methods of preparing carbon dioxide.
7. Show how carbon dioxide is formed in the equations:



Write the ionic form of each of these equations.

8. Write the equation for the reaction of baking-soda with acetic acid (vinegar). What is the visible evidence of chemical change?
9. Write the equation for the preparation of carbonic acid from its anhydride. Rewrite the equation using graphic formulas.
10. What is dry ice? What advantages has it as a refrigerant? Give three other uses of carbon dioxide.
11. Write the equation for the reaction between carbon dioxide and lime-water $\text{Ca}(\text{OH})_2$. What is the visible evidence of chemical change?
12. Write formulas for aluminium carbide, and hydrogen carbide. Give the formulas and uses of silicon carbide and calcium carbide.
13. How many liters of carbon dioxide gas are produced by the reaction of 350 g. of marble (calcium carbonate) with hydrochloric acid? This volume of gas (at standard conditions) will occupy how many liters at 23° C. and 730 mm. pressure.
14. Five liters of carbon dioxide gas as measured at laboratory conditions, 20° C. and 745 mm. pressure are passed into a solution of calcium hydroxide. How many grams of calcium carbonate will be formed?
15. How many grams of calcium carbonate will be dissolved by 38 c.c. of tenth-normal sulphuric acid?
16. It required 40 c.c. of hydrochloric acid to react with 1.462 grams of a sample of baking soda. What is the normality of the acid?

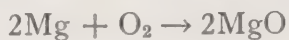
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CHAPTER XVII

OXIDATION AND REDUCTION

OXIDATION (Chapter IV) has been defined as a process in which oxygen combines with an element; it is illustrated by such a reaction as the direct union of a metal with oxygen:



Reduction (Chapter VI) has been defined as a process in which some element removes oxygen from a compound, as is illustrated by the experiment in which hydrogen takes oxygen from copper oxide:



There is, however, a broader and more inclusive conception of oxidation and reduction that includes all reactions in which there is a transfer of electrons. According to this conception, oxygen need not be involved in the process. It should be noted, however, that reactions similar to those just mentioned in which oxygen is added or removed from a substance are included in the definition. In the first equation, for example, electrons are transferred from the magnesium to the oxygen atoms, and in the second equation electrons are transferred from the hydrogen to the copper atoms. According to the new definition *oxidation means that an element gives up electrons (the valence is increased), and reduction means that an element takes electrons (the valence is decreased)*. In the first of the preceding reactions magnesium is oxidized not only because it combines with oxygen, but because it has lost electrons and increased in valence from zero to positive two. In the same reaction oxygen is reduced because it gains electrons and is decreased in valence from zero to negative two. In the second equation the copper is reduced and the hydrogen is oxidized. It is evident that reactions of this type may be classed together as oxidation-reduc-

tion since neither process may occur without the other; that is, electrons can only be given up by one atom if they are accepted by some other atom.

Types of Reaction Which Are Oxidation-Reduction. — 1. *Direct Union.* In Chapter VII we learned that whenever two elements combine there is a transfer or sharing of electrons. All reactions of this kind are included in the oxidation-reduction type. A typical example is:



In this reaction the iron loses electrons and is increased in valence from zero to positive two. Iron is therefore oxidized. The sulphur is reduced because it takes the two electrons from the iron and its valence is decreased from zero to negative two.

2. *Displacement Reactions.* In Chapter XIV, it was stated that in displacement reactions electrons are transferred from a more active element to a less active element. In other words, these reactions are oxidation-reduction. The reaction of an acid (hydrogen ions) with an active metal such as zinc is written in ionic form:



The zinc is said to be oxidized because it gives up two electrons and is increased in valence from zero to positive two. The hydrogen ions are reduced, since they each add one electron. Hydrogen decreases in valence from positive one to zero.

3. *Decomposition Reactions.* We will use the following reaction as an illustration of this type:



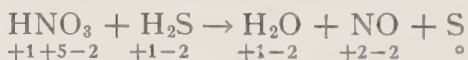
From a study of the valence of each atom in all the substances entering into reaction and in the products, it is evident that chlorine atoms decrease in valence from positive five to negative one. Chlorine is reduced because it takes electrons from oxygen.

Each atom of oxygen gives up the electrons that made it negative, and these become neutral molecules of oxygen gas, O_2 .

Oxygen increases in valence by giving electrons, and so it is oxidized. Many decomposition reactions may be shown to be of this type.

Double Decomposition Reactions Are Not Oxidation-Reduction. — An analysis of double decomposition reactions indicates that there is no change or transfer of electrons in these reactions. The ions of the acid, base, or salt merely recombine to form new products in which each ion has the same valence as in the original reactant. Therefore, double decomposition reactions are not oxidation-reduction.

Balancing Oxidation-Reduction Reactions. — We must now understand that if one atom gives up more (or less) electrons than another atom can take, the number of atoms of each element must be adjusted in such a way that all the electrons given by one element are accepted by the other element. On this principle is based another method for balancing reactions (see method described in Chapter II). The method can be used only for oxidation-reduction reactions, as it is the electron transfer that determines the number of molecules of two of the reactants. An illustration follows which explains this method of balancing equations; the unbalanced equation showing the valence of each element in an oxidation-reduction reaction is as follows:



In this equation the nitrogen atoms add electrons (are reduced) and the sulphur atoms give up electrons (are oxidized). The transfer of electrons may be indicated:



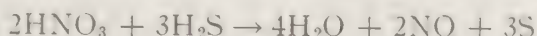
In order to adjust the number of nitrogen and sulphur atoms so that all of the electrons given up by the sulphur atoms are used by the nitrogen atoms, the total number of electrons transferred must be the least common multiple of the number given up and

the number gained. For the equation just written, the least common multiple of 2 and 3 is 6. Therefore, two nitrogen atoms and three sulphur atoms will be required to balance the electron transfer. In other words,

2N^{+5} atoms add 6 electrons to form 2N^{+2}

3S^{-2} atoms add 6 electrons to form 3S^0

Knowing that the equation will balance only when the nitrogen and sulphur atoms are in the ratio of 2 to 3, we may balance the remaining part of the equation by inspection:



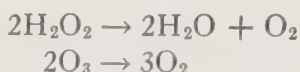
Mastery of this method of determining the ratio of the atoms of the oxidized and reduced elements will simplify the balancing of many complex equations.

The steps involved in using this method to balance oxidation-reduction reactions are summarized as follows:

- (1) Indicate the valence of each element in the equation.
- (2) Write the electron changes and adjust them so as to equalize the gain and loss of electrons.
- (3) Adjust the number of molecules of each reactant to correspond to the electron change.
- (4) Complete the balancing of the equation by inspection.

Oxidizing Agents and Reducing Agents. — It is customary to call the substance which contains an element that can accept electrons (or be reduced) the **oxidizing agent**. This substance causes another element to be oxidized. Many of these substances contain oxygen, but that is not a specific requirement according to the conception which makes the acceptance of electrons the outstanding function of the oxidizing agent. In the equation of the preceding paragraph, nitric acid is the oxidizing agent because N^{+5} accepts electrons to form N^{+2} . In like manner, sulphuric acid is an oxidizing agent because S^{+6} can accept electrons in forming sulphur dioxide, S^{+4} , or other compounds in which sulphur has a lower valence than positive six. Chlorine is an oxidizing agent because the element chlorine, Cl_2^0 , accepts

electrons to form chloride ion, Cl^- . A ferric compound is an oxidizing agent because ferric ions Fe^{+++} , accept electrons to form ferrous ions Fe^{++} . Hydrogen peroxide, H_2O_2 , and ozone, O_3 , are two other interesting oxidizing agents which decompose on exposure to heat and light to form oxygen. If this free oxygen combines immediately with other substances, they are oxidized. The equations to show the decomposition of hydrogen peroxide and ozone are as follows:

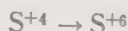
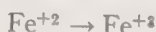


A reducing agent is a substance which contains an element that can give electrons (or be oxidized). This substance causes another element to be reduced. In the balanced equation of the previous section, hydrogen sulphide is the reducing agent because sulphide ion, $\text{S}^{=}$, transfers electrons to the nitrogen atom. Thus the sulphur atom is oxidized while the nitrogen atom is reduced. In like manner, active metals are reducing agents when the metal transfers electrons to another atom in forming a positive ion, as when Zn^0 gives up two electrons to form zinc ion, Zn^{++} . Ferrous ion, Fe^{++} , is a reducing agent because an electron may be given up to form ferric ion, Fe^{+++} .

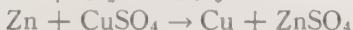
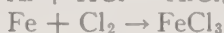
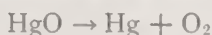
A more detailed study of oxidizing agents and reducing agents will be made as such compounds are mentioned in later chapters. In general, such compounds have great chemical reactivity and many of them have important uses in bleaching such commodities as paper, hair, textiles (Chapter XXXIV), and in antiseptic solutions.

QUESTIONS AND PROBLEMS

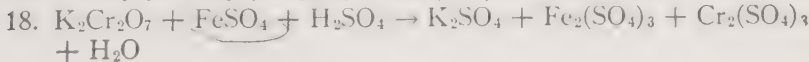
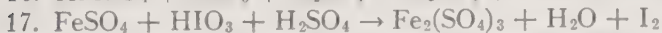
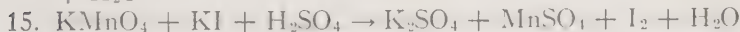
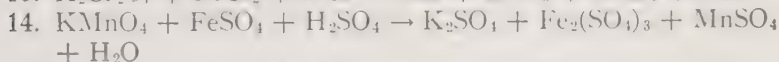
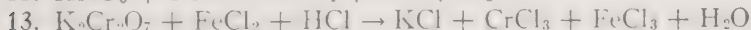
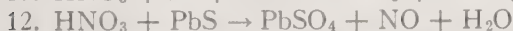
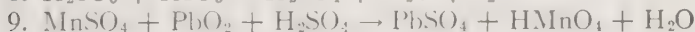
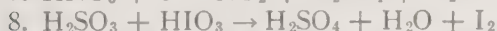
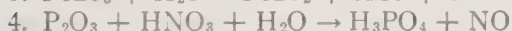
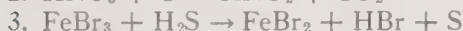
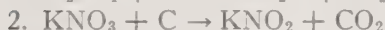
1. Define oxidation and reduction in terms of valence change, and in terms of electron transfer.
2. Tell whether the following changes in valence are oxidation or reduction, and indicate the gain or loss of electrons in the change:



3. Write two equations of each of the following types and tell how each can be considered as an oxidation-reduction reaction:
- direct union of elements
 - displacement
 - decomposition
4. Classify the following reactions as one of the types mentioned in question 3. Balance each equation, showing the electron transfer. What element is reduced and what element is oxidized?



5. Balance the following equations: tell what element is oxidized and what element is reduced; indicate the oxidizing agent and the reducing agent:



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CHAPTER XVIII

THE ATMOSPHERE

THE atmosphere is the name given to the gaseous envelope that surrounds the earth. Although minute quantities of these gases may extend not only throughout our solar system but throughout all space in our galaxy, most of the gaseous envelope is held close to the earth's surface by the force of gravity. In fact the atmosphere is so much more dense at the earth's surface that, when one rises more than three or four miles above sea level, extra oxygen must be supplied. On the other hand, the aurora borealis or northern lights have appeared as high as 500 miles above sea level, which indicates that there is an appreciable quantity of air at this height.

The upper layers of the atmosphere have been studied by observing clouds, by sending radio signals, by the use of unmanned balloons carrying instruments as high as twenty-two miles, and by stratosphere balloons in which men have travelled as high as fourteen miles above the earth's surface. These observations have indicated that above fifty miles the atmosphere contains a large proportion of the lighter gases, hydrogen and helium, and that above 100 miles the atmosphere is ionized or electrically charged. It is through this electrically charged layer of atmosphere that radio waves travel. In the layer called the stratosphere, from eight to twenty-two miles above the earth's surface, there are no winds or air currents.

Personally, we are all most interested in the layer of air lying next to the earth's surface since life is dependent on it. We have learned in previous chapters that air is composed of approximately one-fifth oxygen and four-fifths nitrogen; besides these two gases it contains a small amount of carbon dioxide, of water vapor, and minute quantities of other gases.

The oxygen is the most important constituent since it supports



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EXPLORER II

In a flight sponsored jointly by the National Geographic Society and the United States Army Air Corps, Captain O. A. Anderson and Captain A. W. Stevens ascended in the gondola of Explorer II to an altitude of 72,395 ft. (13.71 miles) and gathered scientific data. The Explorer II was filled with helium gas (*Nat. Geographic*, 69, 59, 1936).

all life by oxidizing certain organic compounds to give energy. Moreover, it is necessary for all burning processes. The nitrogen is inactive chemically and serves to dilute the oxygen, preventing oxidation from becoming too rapid and violent.

Carbon dioxide is continually added to the air by the respiration of animals and plants and by the combustion or burning of organic matter. It does not accumulate in large quantities however because plants use it in the process of photosynthesis in which they combine the carbon dioxide of the air with the water from the soil to form sugars and release the element, oxygen. The free oxygen is breathed out by the plants to replenish the supply in the atmosphere.

Air-Conditioning. — In recent years the process of air-conditioning in public buildings and in private homes has been receiving increased attention. Although to many people the term refers only to air-cooling in the summer time, to the engineer and architect the term includes all of the processes used to make the air in a building more healthful and comfortable. This includes temperature control (heating or cooling), humidity control, ventilation, and cleaning of the air.

Methods of heating buildings have been known since prehistoric times, and are constantly being improved. Although primitive methods of cooling have always been of interest, it is only recently that widespread attention has been given to the problem. In large buildings the air is often cooled by drawing it with a fan through a spray of water. In smaller buildings the air may be drawn into the building at night by means of a ventilating fan, and circulated through the house during the warm day.

The control of humidity in air-conditioning is fully as important as the control of temperature in making a room comfortable. **Absolute humidity**, or the concentration of water vapor in air saturated with moisture, is dependent on the temperature. It may be expressed in terms of the grams of water vapor in a unit volume of air saturated with moisture, or in terms of the partial pressure that the vapor exerts as expressed in millimeters of mercury. Both values are given in Section 3, in the Appendix.

The **relative humidity** is the ratio of the concentration of water vapor present in the air to the concentration of water vapor that the air would contain if saturated at the same temperature (absolute humidity). It is the relative humidity that affects our comfort, because it controls the rate at which perspiration may evaporate from the body, cooling it by the absorption of heat of vaporization.

We often feel uncomfortable in summer, even when the temperature is not excessively high, if the relative humidity is high and perspiration does not evaporate easily. Moreover wet clothes dry slowly, and the accumulation of moisture stimulates the growth of molds and mildew.

When the temperature of the air is lowered without controlling the humidity there is an increase in relative humidity, as may be shown by an example. On a typical warm summer day with a temperature of 86°F. (30°C.) and a relative humidity of 50 per cent, the air contains 50 per cent of 30.4 grams (Appendix, Section 3) or 15.2 grams of moisture in each cubic meter. If this air should be cooled by some means to 68°F. (20°C.) and no effort made to dry the air, it would still contain 15.2 grams of moisture, although air at this temperature is saturated with 17.3 grams of water vapor per cubic meter (Appendix, Section 3). The relative humidity has thus increased to $\frac{15.2}{17.3}$ or 88 per cent. This high relative humidity prevents perspiration from evaporating and thus interferes with body control of temperature and causes discomfort. In many cases the relative humidity becomes even higher because the cooling is accomplished by allowing moisture to evaporate into the air. In modern air-cooled buildings the cooled washed air is dried by passing it through layers of an anhydrous salt, usually calcium chloride or lithium chloride.

In winter the conditions are reversed. The cold outdoor air is saturated when it contains little moisture; if it is heated in buildings the relative humidity is decreased, as an example will indicate. Cold outdoor air at 6°C. (42.8°F.) and a relative humidity of 50 per cent contains 50 per cent of 7.3 (Appendix, Section 3)

or 3.65 grams of water vapor in each cubic meter. If this air were heated to comfortable room temperature (20°C . or 68°F .) without addition of moisture, it would still contain 3.65 grams of water vapor per cubic meter, although the air at this temperature is saturated with 17.3 grams per cubic meter. In other words, the relative humidity has decreased to $\frac{3.65}{17.3}$ or 21 per cent. In this

environment we become cool because the perspiration evaporates readily from the body. By allowing moisture to evaporate in the room, we can increase the relative humidity, and feel warmer and more comfortable without increasing the temperature.

We feel most comfortable and work most efficiently when the room temperature is near 68° to 70°F . and the relative humidity is between 50 and 60 per cent.

Because it is inefficient and expensive to cool or heat great quantities of air and then release them to the outside in ventilating, arrangements are made in most buildings to recirculate most of the air through a building. This practice has led to an intensive study of the properties of stale air, with a hope of artificially making it as stimulating as natural outdoor air on a clear day. It has long been known that the concentration of carbon dioxide in the air of a building rarely becomes high enough to cause any discomfort, and that the depressing and poisoning effect of "bad air" must be due to either an increase in relative humidity from the moisture of the exhaled breath, or to an accumulation of particles of organic matter from the exhaled breath. Most of these particles have an electric charge and it is possible to remove them by the use of a filter charged with electricity. Such a filtration should also be effective in removing any harmful organisms or dust particles, accumulated in the air as it passed through the building. Other methods of reconditioning the air that are being considered include ultra-violet sterilization, ionization of molecules in the air by electric means, and addition of ozone (molecules of O_3) to the air. Better methods of insulation of houses to prevent loss or gain of heat are also being developed. We can hope that soon the air in our homes can be made as healthful and invigorating as that by the seaside or on the mountain.

Air, a Mixture of Gases. — Although the observations described in the foregoing study of the atmosphere and the processes involved in air-conditioning would lead one to conclude that air is a mixture of gases (not a compound), we may briefly review some of the characteristics which definitely prove that the nitrogen and oxygen in the air are not combined but are present as a mixture of gases.

1. Many of the properties of air are similar to those of its chief component gases, nitrogen and oxygen. Both gases are colorless, odorless, and tasteless, and air has these same properties. Air is slightly lighter than oxygen and heavier than nitrogen, that is, its comparative weight is influenced by the presence of each component. The ability to support combustion is a property of oxygen and is not a property of nitrogen. The air possesses this property in modified form. Comparisons such as these may be made in the case of any mixture. For instance, when salt and pepper are mixed, the color, taste, odor, solubility, and even chemical characteristics of the resulting material are the same as those of the single ingredients, modified only by the presence of the other component.

2. The components of the air may be separated by physical means. We have learned that oxygen is prepared commercially by the fractional distillation of liquid air. This process is possible since the molecules of liquid nitrogen become a gas at a lower temperature than molecules of liquid oxygen. Another example of partial separation occurs when air is bubbled through water and the oxygen dissolves in larger proportion than the nitrogen. It follows that air must be a mixture, since this is a partial separation of the nitrogen from the oxygen. This is comparable with the results obtained when water is added to a mixture of salt and pepper and the salt dissolves in preference to the pepper. Still another example of the separation of the components of air is evident when the air is breathed into the lungs and the oxygen diffuses through the membranes into the body, leaving the nitrogen to be expelled with the waste gases. If air were a compound, it would be impossible for the body to obtain the oxygen so easily.

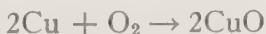
3. A mixture of oxygen and nitrogen resembling air may be

made without any change in energy, although when an electric spark is passed through air a combination of the two gases takes place, and thus through the addition of energy a new compound is formed. This compound, an oxide of nitrogen, is different from air or its component gases. This oxide of nitrogen has a decided odor and dissolves in water, giving the solution a sour taste.

4. The law of definite composition states that every compound has a definite composition by weight (Chapter II). It is evident that a mixture has no definite weight ratio of components. Although the composition of the air is nearly definite because of constant diffusion or mixing of the gases, there are some slight variations that are yet too large to be ignored. Thus the slight difference in the weight ratio of oxygen to nitrogen in samples of air indicates that air is a mixture.

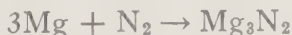
Composition of Air. — As we learned in Chapter IV, chemists have long known that the air consists of approximately one-fifth oxygen and four-fifths nitrogen by volume, and contains a small percentage of water vapor and carbon dioxide. The exact percentage composition of air may be determined by the following method:

A measured quantity of air from which the water vapor and carbon dioxide have been removed is passed through a heated glass tube containing a weighed amount of copper filings. The equation for the reaction that takes place is



The gain in weight of the copper filings, because of the copper oxide formed, is a measure of the oxygen that was present in the air.

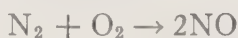
The remaining gases are passed through a tube containing a weighed quantity of heated magnesium, with which the nitrogen combines. The equation for the reaction is



The increase in the weight of this tube is a measure of the nitrogen in the air. Many careful experiments of this type have shown that

air from widely different sources, country and city, mountain and valley, has approximately though not exactly the same composition, namely, by weight, oxygen 23.2 per cent and nitrogen 75.5 per cent; or, by volume, oxygen 21.00 per cent and nitrogen 78.06 per cent.

Rare Gases of the Air. — For many years oxygen and nitrogen were considered to be the only normal components of the air besides carbon dioxide and water vapor. Soon after oxygen and nitrogen were first separated from air, an English chemist, Cavendish, tried to prove that they were the only components by causing the nitrogen of the air to combine quantitatively with the oxygen according to the equation:



He noted that a tiny bubble of gas was left unchanged, but he decided it was too small to be of importance. Years later, in 1892, an English physicist, Lord Rayleigh, announced that he was having difficulty in determining the density of nitrogen gas. In all of his experiments, the weight of a liter of pure nitrogen obtained by decomposing its compounds was lower than the weight of a liter of the nitrogen remaining after the oxygen, carbon dioxide, and water vapor had been removed from the air. Another chemist, Sir William Ramsay, became interested and worked on the problem with Lord Rayleigh. He tried to combine the nitrogen obtained from the air with magnesium, and discovered that about 1 per cent of this gas could not be made to react. A further study of this inactive gas revealed that it was a mixture of five gaseous elements, all new to scientists. They were named argon, helium, neon, krypton, and xenon. Argon is the most abundant, making up 0.94 per cent of the air, while the other four together make up less than 0.04 per cent. These gases are often known as the inert gases, since none of them have ever been made to enter into combination with any other element. However, chemistry has developed some interesting commercial uses for these gaseous elements.

Helium. This gas is named from *helios*, the sun, because, long before it was found in the air by Ramsay, its presence on the sun

was noted by means of an instrument called the spectroscope. The spectroscope could not determine its properties, and the discoverers, guessing it was a metal, used the ending **-ium** to make it correspond to the name for other metallic elements. Like the other rare gases of the air, helium has not been made to form any compounds. It is an extremely light gas, almost as light as hydrogen. Because it is inert and does not burn, it is quite preferable to hydrogen for use in balloons and dirigibles. America is fortunate to have, in Texas and Kansas, natural gas wells that contain 1 per cent of helium. This is the richest source known, and from it the government obtains more than enough of the gas to use in all its dirigibles and balloons. Hospitals use helium gas mixed with oxygen, for patients who have difficulty in breathing. It is especially valuable in the relief of asthma.

We find an important use for helium in the apparatus used by deep-sea divers. In order to give them air to breathe, it is necessary to use high pressure to force the air to the depth at which the diver works. At this pressure, the nitrogen of the air dissolves in the blood. If the diver comes to the surface slowly, the nitrogen gradually leaves the blood and normal conditions are resumed; if however, he rises quickly from the water, the nitrogen gas in the blood suddenly expands, and causes an illness known as "bends." To decrease the danger, the diver may breathe a mixture of helium and oxygen; helium is less soluble in the blood than nitrogen, and so this mixture causes less difficulty from "bends."

Neon. This rare gas has one property that makes it "worth its weight in gold." When neon, in small concentration, is passed into an evacuated glass tube fitted with two electrodes and connected with an electric current, a brilliant red light fills the tube. If a drop of mercury vapor is mixed with the neon, the light becomes blue, and if the blue color is created in a tube of yellow glass, the light is green. These lights have been used extensively for advertising signs. The red light of neon has the property of being visible through fog and mist and consequently is especially adaptable for airport beacons. Moreover, it is interesting to note that these lights, so much more intense and penetrating than ordinary electric lights, require less current.

Argon. Although this element is the most abundant of the rare gases of the atmosphere, less use has been found for it. It is now used extensively to fill electric light bulbs, since the gas will not combine with the metal filaments and tends to prevent their vaporization when heated by the electric current.

QUESTIONS AND PROBLEMS

1. Give four reasons for considering air a mixture.
2. Describe an experiment that may be used to determine the exact composition of the air.
3. How many grams of oxygen and how many grams of nitrogen are present in 1,000 g. of air?
4. Give the physical and chemical properties of helium.
5. Name the five rare gases of the air.
6. Give one use of helium, of argon, and of neon.
7. What factors must be considered in a complete air-conditioning plant?
8. Define the terms—absolute humidity; relative humidity; 100 per cent humidity.
9. If air at 30° C. (86° F.) contains 19 grams of water vapor per cubic meter, what is the relative humidity? Under these conditions, would we be comfortable as to temperature and as to humidity? Explain your answer.
10. When air saturated with water vapor at 10° C. is warmed to 27° C. (80° F.) without addition of water, what is the relative humidity? Under these conditions, would we be comfortable as to temperature and as to humidity? Explain your answer.
11. Warm air saturated with moisture at 32° C. (89.6° F.) is dried until it contains 13.5 grams of water vapor per cubic meter. What is the change in humidity? Explain the effect of this change.
12. Why is it a difficult matter to get the air dry enough in summer and moist enough in winter?

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CHAPTER XIX

NITROGEN. COMPOUNDS OF NITROGEN

Introduction. — All protein matter contains nitrogen in combination with carbon, hydrogen, oxygen, and sometimes other elements. Every cell of our body, many of our foods, and our wool and silk textiles are protein in nature and so contain nitrogen compounds. Thus in order to build tissue, plants and animals must receive nitrogen as a part of their food. The atmosphere is the cheapest and most abundant source of the element nitrogen. Ammonia formed by the destructive distillation of soft coal and deposits of sodium nitrate (NaNO_3) in Chile are other sources of nitrogen compounds. Unfortunately, plants and animals are unable to use as food the abundant supply of nitrogen found in the air. The food, therefore, which builds body tissue must contain nitrogen compounds.

It follows that nitrogen compounds are of great importance in all food and nutrition problems. In the processes of metabolism and digestion, in the cooking of meat, eggs, and milk, nitrogen compounds are undergoing chemical reaction. The changes that occur in nitrogen compounds are of importance also in the textile industry, since the fabrics, as well as many dyes, contain nitrogen compounds. Although only a few of the more important reactions of the simplest compounds of nitrogen can be considered in this chapter, these will form an important basis for later work in physiological, food, and textile chemistry.

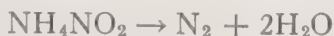
Preparation of Nitrogen. — 1. *From Air.* In Chapter XVIII an experiment is described in which air is passed over heated copper filings. The copper unites with the oxygen in the air, leaving the nitrogen gas, mixed with approximately 1 per cent of impurities. In the laboratory, oxygen is removed from air by burning phosphorus in a beaker of air inverted over water. The

phosphorus oxide which is formed dissolves in the water, leaving nitrogen gas. Although not quite pure, it is suitable for laboratory study. In commercial practice, nitrogen and oxygen are usually prepared in the same operation by the fractional distillation of liquid air (Chapter IV).

2. *From Nitrogen Compounds.* When pure nitrogen is wanted for study in the laboratory, it is usually obtained by the decomposition of pure nitrogen compounds. When sodium nitrite and ammonium chloride are dissolved in water and heated together, the double decomposition reaction forms ammonium nitrite according to the equation:



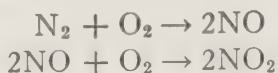
The ammonium nitrite is immediately decomposed into nitrogen gas and water, as shown by the equation



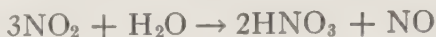
Properties of Nitrogen. — The element nitrogen is a colorless, odorless, and tasteless gas. It is less soluble in water than oxygen. It does not support combustion but at high temperatures and under special conditions, it may be made to unite with oxygen, hydrogen, and certain metals.

Nitrogen Fixation. — Direct union reactions of nitrogen with other elements is the basis of one of the world's greatest chemical industries — **nitrogen fixation**. These are the reactions which convert the nitrogen of the air into useful compounds. The supply of nitrogen compounds in nature does not nearly meet the demand for them. Without these compounds for use in fertilizers, the farms could not grow sufficient food to nourish all of the people of earth. Moreover, the explosives used in war, and in engineering and mining depend on the instability of nitrogen compounds. The basic substances needed in the manufacture of dyes, textiles, and drugs are nitrogen compounds. Because of their importance, many processes of nitrogen fixation have been developed. The most important of these will be described briefly.

1. *By Direct Union of Nitrogen and Oxygen.* This process was the first to be developed and used commercially. When an electric spark is passed through the air, nitric oxide is formed, some of which is immediately oxidized to nitrogen dioxide. The following equations illustrate the two reactions:

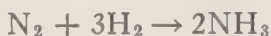


Neither of these oxides are acid anhydrides. However, the nitrogen dioxide will undergo a reaction with hot water to form nitric acid according to the equation:



The nitric oxide formed is again oxidized to nitrogen dioxide as the process continues. These reactions occur in every electric storm; the lightning causes some of the nitrogen and oxygen of the air to combine forming oxides of nitrogen. These dissolve in the rain and sink into the soil where they react to form nitrates, which act as fertilizer for plants.

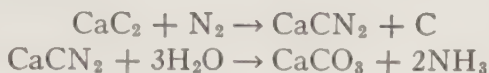
2. *Direct Union of Nitrogen and Hydrogen.* The Haber-Bosch process of nitrogen fixation depends upon the reaction:



The nitrogen and hydrogen gases, under pressure and heated to approximately 500°C ., are passed over an active catalyst. One of the difficulties encountered in the preparation of ammonia by this method is the reversibility of the reaction just given; that is, at the temperature required for the direct union of nitrogen and hydrogen, some decomposition of the ammonia takes place. It is necessary, then, to control the temperature and the pressure in such a way as to obtain the greatest yields of ammonia with the least decomposition of the compound. Also, the choice of a suitable catalyst has been a problem in the development of this method for making ammonia. If the ammonia is to be used for plant growth, it must be converted into a soluble salt, such as ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$, that may be used as a fertilizer.

3. *By Reaction between Nitrogen and Calcium Carbide.* At high

temperatures nitrogen combines with calcium carbide to form a compound called calcium cyanamide CaCN_2 . This compound reacts with steam to form ammonia. The following equations illustrate the reactions:

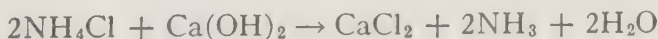


The cyanamide process furnishes a valuable and inexpensive method for nitrogen fixation.

4. *Nitrogen Fixation by Plants.* Certain bacteria which thrive on the roots of leguminous plants, such as peas, clover, and alfalfa, have the ability to use atmospheric nitrogen. These nitrifying bacteria are present in some soils and not in others. When the leguminous crop is planted, the farmer frequently inoculates the field with soil which is known to contain nitrifying bacteria. This furnishes an important and necessary element for the rapid growth of plants, because the bacteria use the atmospheric nitrogen in forming nitrates which, in turn, feed the leguminous plants. After a time, the legumes are plowed into the soil and leave their store of nitrogen as a food for other plants. It is in this way that rotation of crops fertilizes the soil.

COMPOUNDS OF NITROGEN

Preparation of Ammonia. — We have learned that ammonia gas is obtained commercially by the Haber-Bosch process of nitrogen fixation. It is obtained also as a by-product in the destructive distillation of soft coal. For laboratory study, ammonia gas is prepared by the decomposition of ammonium hydroxide, which in turn may be prepared by a double decomposition reaction of an ammonium salt with a base as shown by the following equation:



Since the reaction will occur with any ammonium salt and any soluble base, the ionic form may be written:



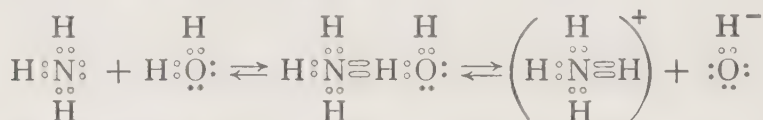
Properties of Ammonia. — Ammonia is a colorless gas with a penetrating odor. The fact that it condenses to a liquid at -33°C . makes it a valuable refrigerant. Ammonia gas dissolves in water and reacts with it to form a weak base, ammonium hydroxide. When heat is applied to the solution, the reaction becomes reversible and ammonia gas escapes. Thus in a solution of ammonium hydroxide there are two sets of equilibria, the one between the base and its ions and the other between the base and the products of decomposition.

This may be written in equation form as follows:



The direction of this reversible reaction depends on temperature, pressure, and concentration of ammonia.

Coördinate valence is shown in the reaction of ammonia with water; the nitrogen atom has two unshared electrons which it shares with the hydrogen atom of water as shown by the following graphic formulas. The ammonium hydroxide formed by the reaction is a weak base and shows electrovalence as it separates into ammonium and hydroxyl ion:



When ammonia and hydrogen chloride gases are mixed, they combine to form ammonium chloride as a dense white cloud. The equation for the reaction is as follows (see graphic form, Chapter XII):



In a similar way ammonia reacts with other acids to form white crystalline salts. Ammonium salts are formed also by reaction of the base with an acid, as illustrated by the equation



Test for Ammonia Gas and Ammonium Ion. Ammonia gas may be recognized by its odor and by its effect upon moist litmus-paper. Ammonia gas dissolves in the moisture, forming am-

monium hydroxide. Since this is a base, it gives a blue color to the litmus. Ammonium salts may be detected by the formation of ammonia gas when a base is added to the salt, as shown by the equation:



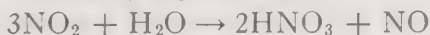
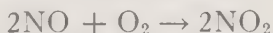
or in ionic form:



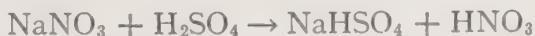
Preparation of Nitric Acid. — 1. *Oxidation of Ammonia to Nitric Acid.* A commercial process for making nitric acid uses the ammonia which is made by direct union of nitrogen and hydrogen. Oxidation occurs when a mixture of ammonia and air are in contact with a catalyst at approximately 800° C. The reaction is indicated by the equation:



The oxide of nitrogen, NO, is readily oxidized in air to nitrogen dioxide, NO₂, which in turn reacts with water to form nitric acid. The following equations show these reactions:



2. *Nitric acid may be made* from Chile saltpeter, NaNO₃, by its reaction with sulphuric acid. The following equation shows the reaction:



Since sulphuric acid has a high boiling-point, it is not vaporized when the mixture is heated. The reaction goes to completion as nitric acid is distilled into a separate container. This method is used for the preparation of nitric acid for study in the laboratory (Fig. 29).

Properties of Nitric Acid. — 1. *Acid Action.* Nitric acid is one of the most highly ionized acids. In a tenth-molar solution it is 96

per cent ionized, and in a hundredth-molar solution it is 99 per cent ionized. Consequently, it has all the properties of a strong acid. In other words, the dilute solution of nitric acid is very sour,

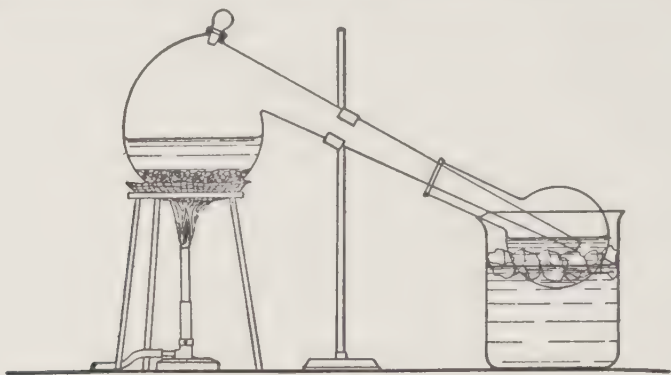
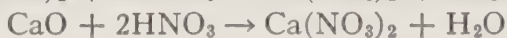
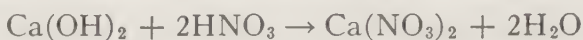
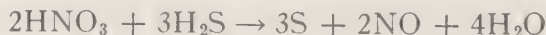
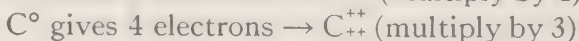
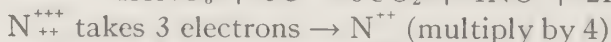


FIG. 29. Preparation of Nitric Acid

changes blue litmus to red, neutralizes bases, and reacts with oxides of metals, as shown by the following typical reactions:

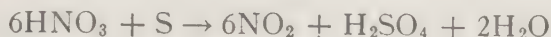


2. Oxidizing Action. In the previous chapter nitric acid was mentioned as one of the best of oxidizing agents. In oxidation-reduction reactions, nitrogen, N^{+++} , in nitric acid is reduced to any lower valence, as in the formation of $\text{NO}_2(\text{N}^{++})$, $\text{NO}(\text{N}^{++})$, $\text{N}_2(\text{N}^0)$, or $\text{NH}_3(\text{N}^{\equiv})$. The following equations are typical of some of the oxidation-reduction reactions of nitric acid:

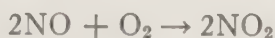


In each of these oxidation-reduction reactions nitric acid acts as an oxidizing agent through the reduction of the nitrogen atom from a valence of positive five in nitric acid to a valence of positive two in nitric oxide NO.

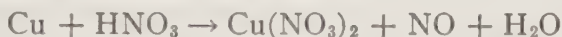
A concentrated solution of nitric acid is a stronger oxidizing agent than the more dilute solution, and in most reactions the nitric acid is reduced only to the brown gas nitrogen dioxide NO_2 . An equation for the reaction of concentrated nitric acid with sulphur is:



Even in reactions in which the dilute acid is used and nitric oxide is formed, some brown nitrogen dioxide is usually observed because of the oxidation of the colorless nitric oxide by the air, as in the reaction

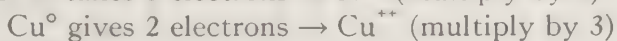
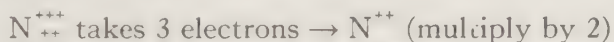


3. *Action with Metals.* Because of its oxidizing action, nitric acid will react with nearly all metals. Only gold and platinum resist its action. When concentrated acid is added to a metal, the gas nitrogen dioxide is formed; when more dilute acid is used, nitric oxide forms as the reduction product of the acid. A typical equation (unbalanced) follows:

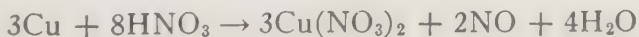


In this reaction, nitric acid acts in two capacities: first, as an oxidizing agent to oxidize the copper, and then as an acid to furnish nitrate ions for the copper ions.

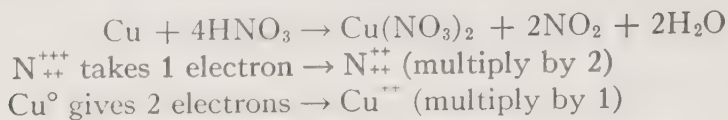
Balancing reactions of this type adds a new problem. The electron change is as follows:



The multiples indicate the ratio of two molecules of nitric acid as an oxidizing agent with three molecules of copper as a reducing agent. Consequently in the product, there appears $3\text{Cu}(\text{NO}_3)_2$ and 2NO . The reduction of two molecules of nitric acid forms the nitric oxide, 2NO , but it requires six more molecules of nitric acid to form copper nitrate, $3\text{Cu}(\text{NO}_3)_2$. Therefore in all, eight molecules of nitric acid are necessary to balance the equation. The balanced equation then reads

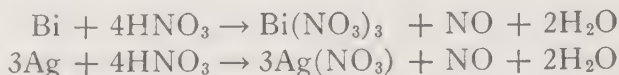


The equation for the reaction of concentrated nitric acid with copper is balanced in a similar manner.

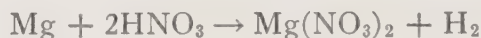


Two molecules of nitric acid are reduced to nitrogen dioxide, 2NO_2 , and the equation required also, two molecules of nitric acid to form copper nitrate, $\text{Cu}(\text{NO}_3)_2$. Therefore in all, four molecules of nitric acid are needed in balancing the equation.

Nitric acid reacts in a similar manner with nearly all metals below hydrogen in the electrochemical series. For example, other typical reactions are:



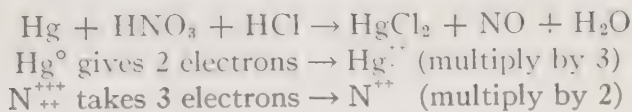
The action of nitric acid with metals above hydrogen is variable depending on the concentration of the acid and the activity of the metal. Active metals may react with dilute nitric acid in the same manner as with other acids, to displace hydrogen:



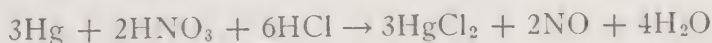
When more concentrated acid is used or when the metal is less reactive, complicated reactions may take place between the reducing agent, hydrogen, and the oxidizing agent, nitric acid. In any case the nitrate of the metal is formed, but the other products are so variable that they cannot be included in any one simple equation.

Aqua Regia. — The laboratory reagent that is most powerful in reacting with the inactive metals is a mixture of nitric acid and hydrochloric acid. Since the noble metals (gold and platinum), which are not attacked by any other acids, are dissolved by this mixture, it is known as *aqua regia* ("royal water"). Other metals as well as gold and platinum are attacked by aqua regia. The reaction is of the oxidation-reduction type, since the metal goes

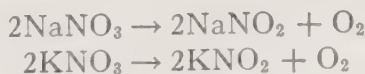
into solution as the chloride and the nitric acid is reduced to nitric oxide NO. The following equation is typical of the reaction:



In this equation, two molecules of nitric acid act as an oxidizing agent with three molecules of mercury. The balanced equation reads



Nitrates. — The salts of nitric acid are crystalline compounds soluble in water. They decompose rather easily when heated. Decomposition of sodium and potassium salts occurs according to the equations:



The decomposition of ammonium nitrate is according to the equation

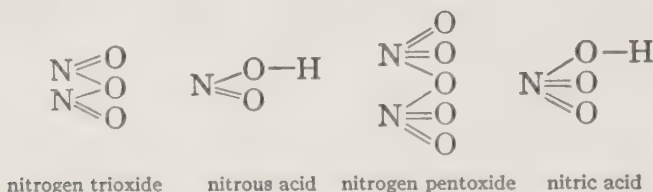


The decomposition of all other nitrates gives the oxide of the metal. A typical equation is as follows:

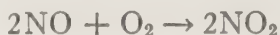


Test for Nitrate Ion. The presence of nitrate ion in a water solution may be detected by a characteristic reaction known as the "brown-ring" test. When ferrous sulphate solution is mixed in a test tube with a solution containing the nitrate ion, and concentrated sulphuric acid is poured slowly down the side of the tube to form a layer beneath the mixture, a characteristic brown ring forms on the surface of the sulphuric acid between the two layers of liquid. The sulphuric acid reacts with the nitrate, forming the compound NO. This oxide in contact with ferrous sulphate forms a brown compound, $\text{FeSO}_4\cdot\text{NO}$.

Oxides of Nitrogen. — Nitrogen shows five different valences as indicated by the formulas for the oxides: N_2O , NO , N_2O_3 , NO_2 , and N_2O_5 . Nitrogen trioxide, N_2O_3 , is the acid anhydride of nitrous acid, HNO_2 , and nitrogen pentoxide, N_2O_5 , is the acid anhydride of nitric acid, HNO_3 . Note that in the graphical formula for the acid, the valence of nitrogen is the same as in its acid anhydride:



The oxides, NO and NO_2 , are formed by reaction of reducing agents with nitric acid. Nitrogen dioxide is a brown gas and is a product of the reaction:



Nitrous oxide, N_2O , is formed by decomposition of ammonium nitrate:



A mixture of nitrous oxide and oxygen is an anesthetic. It is efficient in acting quickly, but its hysterical after effects are somewhat unpleasant.

QUESTIONS AND PROBLEMS

1. Why is nitrogen important in the study of chemistry?
2. What are the sources of nitrogen in nature?
3. What is meant by the term *fixation of nitrogen*? Briefly describe four methods for nitrogen fixation, writing an equation for each. Which method is most important in the United States? Why are these methods important?
4. How may nitrogen be obtained from ammonium nitrite? Write the equation.
5. Diagram the apparatus used in laboratory for the preparation of ammonia gas. What is the purpose of each substance used? Write an equation for the reaction. Practice using this method by writing

another equation for the reaction of another ammonium salt with some other base.

6. How do we know that ammonia gas reacts with water? Write complete equilibria equations.
7. How many liters of ammonia gas are formed by reaction of 150 g. of ammonium chloride with calcium hydroxide?
8. What is visible when ammonia and hydrogen chloride gases are brought in contact? Write an equation for the reaction. Write an equation to prepare the same salt by a double decomposition reaction.
9. Write an equation and describe a test for ammonium ion in ammonium sulphate.
10. Diagram the apparatus used in the laboratory for the preparation of nitric acid. Explain the purpose of each substance used. Write an equation for the reaction. Why does the reaction go to completion?
11. As a strong acid, what properties are characteristic of nitric acid?
12. Write an equation to show the oxidizing action of nitric acid upon a metal, and upon a non-metal. Explain why each reaction is oxidation-reduction. What element is oxidized, and what element is reduced?
13. What is aqua regia? Write the equation for its reaction in dissolving mercury. Why is the reaction of the oxidation-reduction type?
14. How many liters of nitrous oxide, N_2O , will be formed by decomposition of 420 g. of ammonium nitrate?
15. How many grams of ammonium nitrite will be required in the preparation of twenty-five liters of nitrogen gas?
16. Write structural formulas for the five oxides of nitrogen.
17. Describe a test for a nitrate.
18. Twenty-two c.c. of .148 N sulphuric acid neutralizes 18 c.c. of ammonium hydroxide. What is the normality of the ammonium hydroxide solution?
19. Concentrated nitric acid is 12 N. How many grams of copper nitrate will be formed by the reaction of 20 c.c. of 12 N nitric acid with copper? How many liters of nitrogen dioxide gas will be formed?
20. Twenty-five liters of oxygen gas at $18^\circ C$. and 735 mm. pressure is used in the oxidation of ammonia to nitric oxide, NO . How many liters of nitric oxide (standard conditions) will be formed?

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CHAPTER XX

SULPHUR. COMPOUNDS OF SULPHUR

WHEN we consider the numberless ways in which sulphur and its compounds assist us every day, we are certain that it should be studied as one of the most important elements. The protein of the body contains sulphur in combination with other elements, hence it is a necessary constituent of our foods. Its compounds also are necessary in many commercial operations, such as the bleaching of paper pulp, the vulcanization of rubber, the manufacture of fertilizers, and the manufacture of synthetic fibers. Compounds of sulphur are used in household refrigeration, in fumigation, and in the manufacture of matches, dyes, explosives, paints, petroleum products, and many other substances.

Occurrence. — Since sulphur is chemically inactive at ordinary temperatures, it frequently occurs in nature in a free or uncombined state. For many years the sulphur supply of the world was obtained from Sicily and Italy, where it is mixed with volcanic rocks. Recently the United States has been obtaining more than enough sulphur to supply its needs from deposits in Texas and Louisiana. These deposits are between 500 and 700 feet underground and were discovered while drilling for oil. Besides the free sulphur deposits, many metal sulphides occur in nature, such as those of iron, zinc, and lead. A few elements, notably calcium, barium, and strontium, occur as sulphates.

Preparation of Sulphur. — In Sicily and Italy the sulphur deposits are so near the surface that pure sulphur is obtained by a simple process. The volcanic rocks containing sulphur are made into huge piles and set on fire. The burning of a part of the sulphur generates heat enough to melt the surrounding sulphur, which flows away from the soil and rock and is collected as it solidifies.

In America, although the sulphur is so far underground and is overlaid with large deposits of clay and sand, pure sulphur is obtained at such a low cost that in the production we can compete successfully with Sicily. This is because of an ingenious method of extraction devised by Dr. Herman Frasch in which superheated steam is used to melt the sulphur (Fig. 30). Wells are drilled down

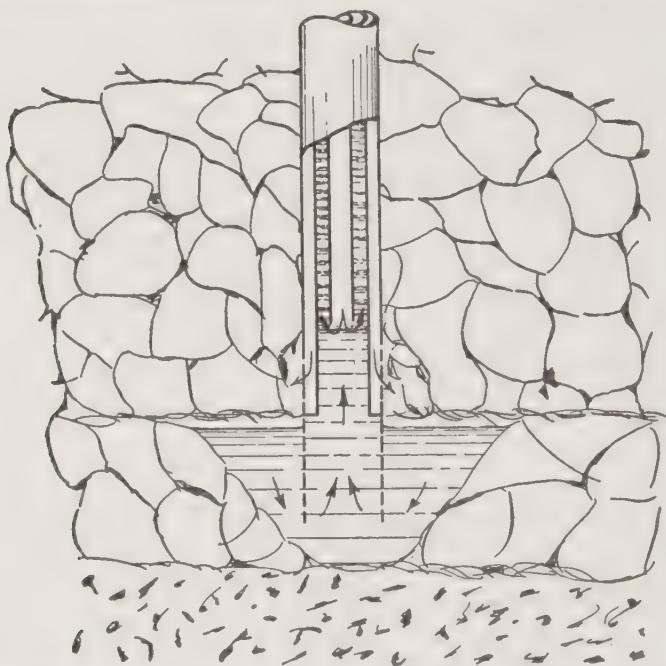


FIG. 30. Diagram to Show the Frasch Process for Obtaining Sulphur

to the deposits and three or four concentric pipes are inserted. Superheated steam is sent down the outer of these pipes and compressed air is forced down the center pipe. The sulphur, melted by the steam, collects at the bottom of the well and by means of the compressed air, is forced up one of the middle pipes as a froth of molten sulphur, water, and air. This mixture is pumped into a tank in which the sulphur solidifies and sinks while the air and water are run off at the top. Froth is added until the sulphur fills the vat. Sulphur obtained by this process is about 99 per cent pure.

Properties of Sulphur. — *Physical.* Some of the properties of sulphur are probably familiar, such as its yellow color, low melting-point, and insolubility in water. From laboratory contact with it one learns that sulphur, like carbon, may be made into different allotropic forms. Under ordinary conditions, the sulphur most familiar is in the form of tiny diamond-shaped or **rhombic** crystals. If sulphur is dissolved in carbon disulphide and the liquid is allowed to evaporate slowly, the crystals of sulphur separate and grow large enough so that the rhombic form may be recognized.

When sulphur is heated until it is just melted and then cooled, the crystals that form are long and needle-like, or **monoclinic**. If these crystals are kept at the temperature of boiling water they will remain monoclinic indefinitely, but under ordinary temperature and pressure they are not stable and slowly revert to the rhombic form. When sulphur is heated beyond the melting-point, it passes through several changes before it begins to boil. When first melted it is a thin yellow liquid that pours easily. At a higher temperature it becomes dark and so viscous that it will not pour from the container. With continued heat, it thins a little and boils at 444.6°C . If this boiling liquid is cooled suddenly by pouring it into cold water, a rubber-like form of sulphur results which is called **plastic** sulphur. The sudden cooling of the hot liquid prevents crystallization, and the plastic sulphur is amorphous. At room temperature this form of sulphur, like the monoclinic, gradually changes into the more stable rhombic form.

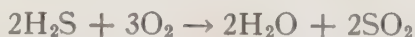
Chemical. The chemical properties of sulphur have made it interesting to scientists and their predecessors ever since the beginning of history. The ease with which it burns, the heat of the reaction, the blue color of the flame, and the suffocating odor of the sulphur dioxide gas thus formed not only gave Old Testament writers their terrifying symbol of "fire and brimstone" but suggested its use as a reagent for the alchemists and as a medicine and fumigating agent for medical practitioners.

COMPOUNDS OF SULPHUR

Hydrogen Sulphide and Hydrosulphuric Acid. — Whenever a sulphide reacts with an acid, hydrogen sulphide gas is formed. In the laboratory preparation of this gas, iron sulphide is usually used because it is the least expensive and most available salt. The equation for the reaction is as follows:



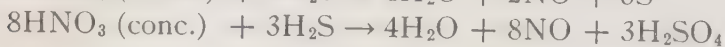
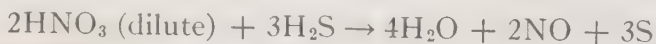
Hydrogen sulphide gas is colorless, has a disagreeable odor, and is somewhat poisonous, causing headache and even fainting. The gas will burn, and since both constituents are easily oxidized, the following reaction takes place when hydrogen sulphide burns in excess of oxygen:



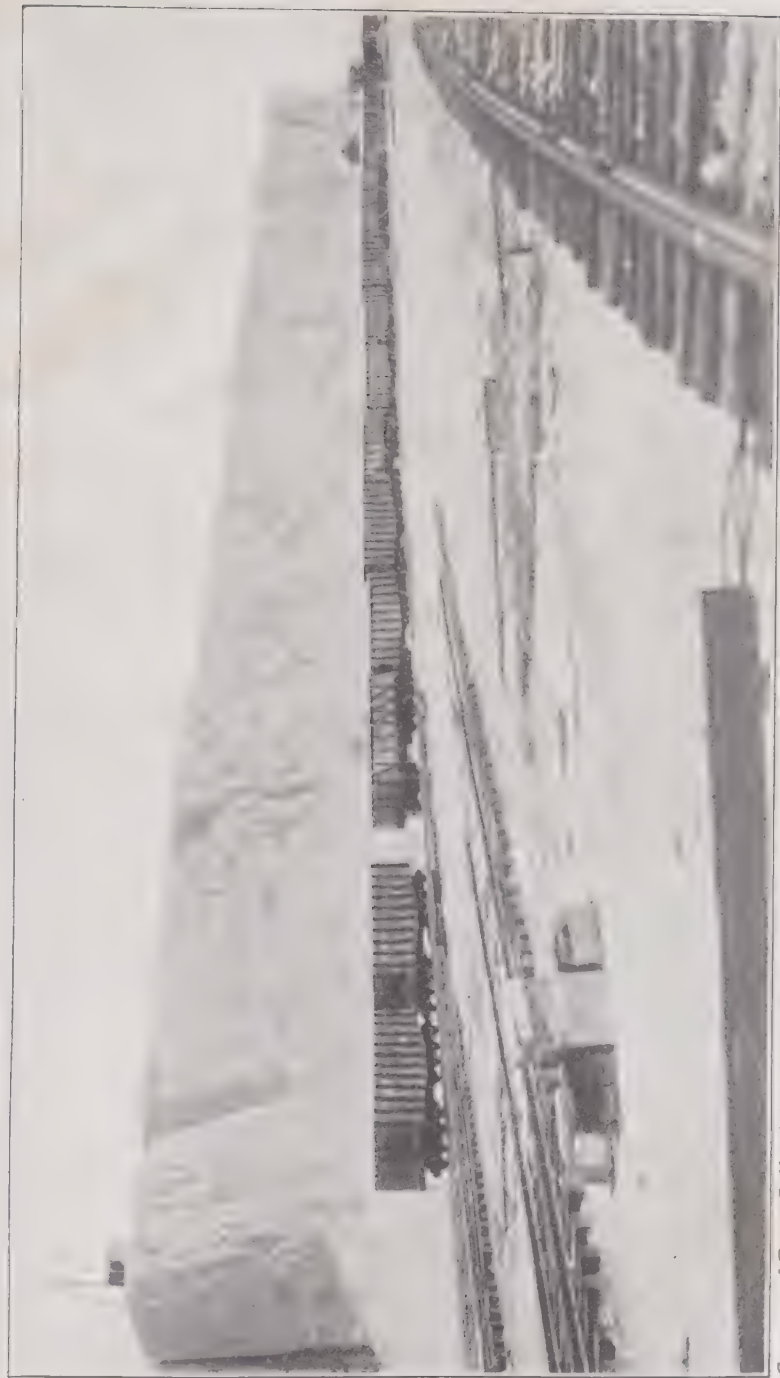
If hydrogen sulphide burns in a limited amount of oxygen, the sulphur is deposited as an element and only the hydrogen combines with oxygen, as shown in the following equation:



Besides being easily combined with the oxygen of the air, the sulphur in hydrogen sulphide may be oxidized (increased in valence) by oxidizing solutions such as nitric acid. In these reactions the sulphur may be increased in valence from negative two in hydrogen sulphide to zero in the element sulphur, to positive four in sulphur dioxide, or to positive six in sulphuric acid. This is shown in the following typical reactions:



Hydrogen sulphide gas dissolves in water, forming hydrosulphuric acid, which has the properties of a weak acid. When the gas or its water solution is used in contact with certain salts, metallic sulphides are formed. If the sulphides are insoluble, the

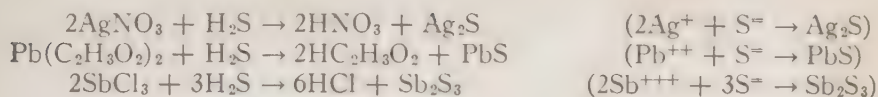


Courtesy of Texas Gulf Sulphur Company

LOADING SULPHUR

The extraction of sulphur by the Frasch process is described in Chapter XX. The melted sulphur is pumped into huge vats in which it solidifies. The photograph shows cars being loaded from one of these vats.

reactions go to completion. The complete equations and the ionic equations are as follows:

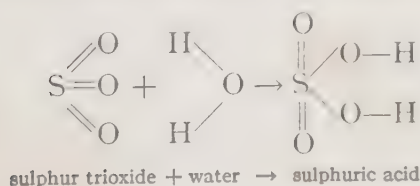
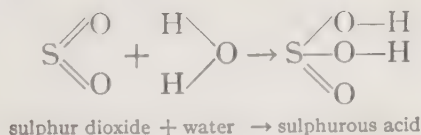


Many sulphides have characteristic colors; for example:

FeS	black	Sb ₂ S ₃	orange-red
Ag ₂ S	black	HgS	red
CdS	yellow	As ₂ S ₃	yellow
PbS	black	ZnS	white

Black silver sulphide is the compound responsible for the tarnish on silverware. It forms when silver is exposed to sulphur compounds in the food or in gases evolved from burning coal. Some sulphides are so stable and have such a clear and attractive color that they are used as paint pigments. Chemists make use of the color of the sulphides of metals by forming them in testing for metallic ions, or in testing for hydrogen sulphide gas. The **test for hydrogen sulphide** is made by bringing a piece of filter paper moistened with lead acetate solution in contact with the gas. A dark deposit of lead sulphide is formed on the paper (see equation in the preceding paragraph).

The Oxides of Sulphur. — Sulphur dioxide, SO_2 , is the acid anhydride of sulphurous acid, and sulphur trioxide, SO_3 , is the acid anhydride of sulphuric acid. The relationship of the acid anhydride to the acid is shown by the following equations using graphic formulas:



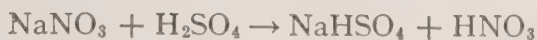
Sulphuric Acid and Its Anhydride. — When sulphur is burned in the air, sulphur dioxide, SO_2 , is formed, with traces of sulphur trioxide, SO_3 . When sulphur dioxide is oxidized in the presence of a catalyst, sulphur trioxide is formed. This reaction is of considerable importance, since sulphur trioxide is the anhydride of sulphuric acid. When sulphuric acid is made by the contact process, sulphur dioxide and oxygen gases are led through a tube filled with a catalyst (finely divided platinum) and held at a temperature of approximately 400°C . Under these conditions, the following reaction occurs:



Although sulphur trioxide is the acid anhydride of sulphuric acid, the gas, SO_3 , is not readily dissolved in water. Sulphur trioxide may be converted into sulphuric acid by passing the gas into a concentrated solution of sulphuric acid. The sulphur trioxide then combines with the water present in the concentrated sulphuric acid; water is added to the mixture to ensure a continuous process of the reaction of sulphur trioxide with the water of the concentrated sulphuric acid. The acid formed by the contact process is always a concentrated sulphuric acid. The process has been considered expensive because of the use of platinum as a catalyst. Other less expensive catalysts, such as vanadium oxide, have been used successfully.

Sulphuric acid may be made by another method in which sulphur dioxide, oxygen, and steam react in the presence of oxides of nitrogen. Such a reaction must take place in a suitable chamber from which the gases cannot escape. The chambers are lined with lead, a metal which has slight chemical reaction with sulphuric acid. In these lead chambers the gases are mixed in suitable proportions and under conditions in which the sulphur dioxide, oxygen, and steam unite to form sulphuric acid. A dilute acid is formed by this process; however, the acid is a valuable product for many commercial operations.

It will be recalled that nitric and hydrochloric acids were prepared from the corresponding salts by double decomposition reactions with sulphuric acid, as shown by the equations:



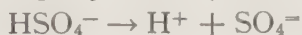
If we had a suitable acid, it might be possible to prepare sulphuric acid from calcium sulphate by a double decomposition reaction similar to those given for other acids; for example:



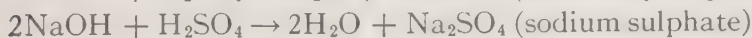
But there is no inexpensive acid (HX), known to chemists, which would make this reaction go to completion and thus liberate sulphuric acid from its salt. For this reason sulphuric acid is made from the elementary substances; that is, the process involves the oxidation of sulphur to sulphur trioxide or to some compound in which the valence of sulphur is positive six, and subsequent reaction of the product with water.

Sulphuric acid has an unlimited variety of uses because of four outstanding properties:

1. Sulphuric acid in dilute solution is **highly ionized**, therefore the properties dependent on hydrogen ion concentration are important. The ionization of sulphuric acid may be shown by the equations

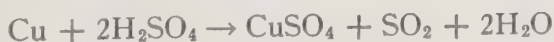


When sulphuric acid is neutralized by a base, either the acid salt or the normal salt may be formed as shown by the following equations:



Dilute sulphuric acid reacts with metals above hydrogen in the electrochemical series, hydrogen gas being formed by the transfer of electrons from the metal to the hydrogen ion.

2. In concentrated solution, sulphuric acid is **an oxidizing agent**. It reacts with metals in a similar way to the nitric acid just studied (Chapter XIX). The equation for the reaction of the acid with copper is the following:



Concentrated sulphuric acid will react in this way with nearly all metals (compare with dilute sulphuric acid) regardless of their position in the electrochemical series. It oxidizes non-metals, also, as illustrated by its reaction with carbon in the following equation:



3. Because sulphuric acid has a high boiling-point, it **liberates other acids from their salts**. This makes sulphuric acid useful in the preparation of many volatile acids. The equations for typical reactions follow:



The first of the reactions just given goes to completion because at ordinary temperature and pressure carbonic acid is unstable and carbon dioxide gas escapes. The other reactions would be reversible unless precautions are taken to remove the acids from the reacting materials.

4. Concentrated sulphuric acid **absorbs water**. It will take moisture from the atmosphere and from organic matter. Wood, paper, and sugar in contact with sulphuric acid have the water removed from them, leaving carbon. In the device called a desiccator (Fig. 31) the chemist makes use of the absorption of water by sulphuric acid. The air enclosed over sulphuric acid in a desiccator is dry. Hence when chemicals are placed in the desiccator, the last traces of water may be removed from them and they remain dry.

Salts of Sulphuric Acid. — A few of the important salts of sulphuric acid are the following:

$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (Epsom salts)

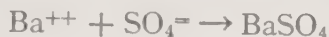
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (blue vitriol)

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum)

$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (alum)

Most sulphates are soluble in water, but barium sulphate, BaSO_4 , is a white, insoluble compound. It is a white paint pigment. The

test for sulphate ion is made by adding a solution of a barium salt to a solution containing sulphate ion. The white precipitate, barium sulphate, BaSO_4 , is formed, insoluble in hydrochloric acid. The following ionic equation shows the reaction:



Sulphurous Acid and Sulphur Dioxide. — While sulphuric acid is much more important than its anhydride, the opposite is true of sulphurous acid. Sulphurous acid is a weakly ionized and un-

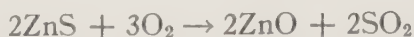


FIG. 31. Desiccator

stable acid decomposing easily into water and sulphur dioxide. The anhydride, sulphur dioxide, may be prepared by four different methods.

1. *By Burning Sulphur.* Sulphur oxidizes to form sulphur dioxide. Since sulphur is found in such abundance, this is the usual commercial method for making sulphur dioxide.

2. *By Burning Sulphides.* This method is used where metallic sulphides are more abundant than sulphur. The equation for the burning of zinc sulphide is as follows:



3. *By the Reaction of a Sulphite with Acid.* This is often used as a laboratory method for preparation of sulphur dioxide. The equation is as follows:



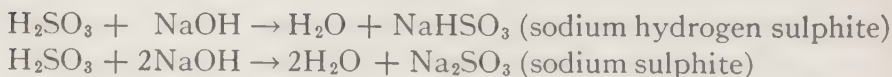
4. *By the Reaction of a Metal with Concentrated Sulphuric Acid.* The reaction has been explained in a previous section. Such a reaction is the following:



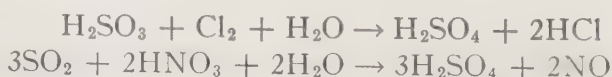
Sulphur dioxide is the acid anhydride of sulphurous acid. The gas combines with water forming a weak acid,



When sulphurous acid is neutralized by a base, either the acid salt or the normal salt may be formed, as shown by the following equations:



Because of the tendency of sulphurous acid to form sulphuric acid, a solution of sulphur dioxide may be a reducing agent. Typical reactions are the following:




There are several properties which make sulphur dioxide useful

in the industries. It is a fair bleaching agent and is used to bleach textiles, dried fruit, and canned corn. The fact that sulphur dioxide liquefies easily makes it valuable as a refrigerant. Sulphurous acid is toxic to plant and animal organisms and so may be used as a disinfectant. As a chemical reagent sulphur dioxide is used in the manufacture of sulphuric acid, of sulphites, and of dyes, and in the refining of oil and the tanning of leather.

QUESTIONS AND PROBLEMS

1. Outline briefly the two methods of mining sulphur. Where is each used?
2. How are the three allotropic forms of sulphur distinguished from each other? State briefly the method of preparing each form in the laboratory.
3. Write the equation for the preparation of hydrogen sulphide gas from ferrous sulphide. What is the type of reaction? What compound is formed to make the reaction go to completion?
4. Write equations for the following reactions of hydrogen sulphide and tell what may be observed when each reaction occurs:
 - (1) incomplete oxidation of hydrogen sulphide
 - (2) complete oxidation of hydrogen sulphide
 - (3) reaction of hydrosulphuric acid with each of the salts: cadmium chloride, lead acetate, silver nitrate
 - (4) oxidation of hydrogen sulphide to sulphur by concentrated nitric acid.
5. Make a comparison of the three acids of sulphur by filling in the blanks of the following table:

	<i>Sulphuric</i>	<i>Sulphurous (Sulphur Dioxide)</i>	<i>Hydrosulphuric (Hydrogen Sulphide)</i>
Formula for acid			
Formula for acid anhydride			
Formula for potassium salt			
Oxidizing or reducing agent			

6. Write equations for the following reactions of sulphuric acid and tell what may be observed when each occurs:
 - (1) dilute sulphuric acid with aluminium
 - (2) concentrated sulphuric acid with zinc
 - (3) dilute sulphuric acid with sodium hydroxide (lye) to form a normal salt; to form an acid salt
 - (4) concentrated sulphuric acid with carbon
 - (5) concentrated sulphuric acid with copper; with silver
 - (6) concentrated sulphuric acid with sodium chloride (salt) and with sodium nitrate.
7. Write the formula for blue vitriol, Epsom salt, alum, brimstone.
8. Describe the reaction of concentrated sulphuric acid on organic compounds (starch, sugar). What property of sulphuric acid does this illustrate?
9. Describe the commercial method for the preparation of sulphuric acid.
10. Write equations to illustrate the preparation of sulphur dioxide by the following methods, and classify each as a commercial or laboratory method:
 - (1) burning sulphur
 - (2) burning zinc sulphide
 - (3) sodium sulphite with an acid
 - (4) concentrated sulphuric acid with copper.
11. What properties of sulphuric acid are of commercial importance?
12. How many grams of ferrous sulphide will be formed when sulphur combines with 25 grams of iron?
13. How many liters of hydrogen sulphide gas will be formed by the reaction of 80 grams of ferrous sulphide with hydrochloric acid?
14. How many liters of oxygen gas will be required for the complete oxidation of twenty-five liters of hydrogen sulphide gas?
15. Describe a test for sulphate ion in potassium sulphate. Write equation for the reaction.
16. Describe a test for sulphide ion, starting with zinc sulphide. Write equations for all reactions involved.
17. Find and rewrite the oxidation-reduction reactions in this chapter. In each reaction, what is the oxidizing agent and the reducing agent; what is oxidized and what is reduced?
18. How many grams of sodium sulphate will be formed when sulphuric acid reacts with 520 c.c. of 0.4 N sodium hydroxide?

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CHAPTER XXI

THE PERIODIC TABLE. STRUCTURE OF THE ATOM

IN the study of the electronic structure of the atoms (Chapter VII) we learned that they are composed of the three units, neutrons, protons, and electrons. The neutrons and protons make up the nucleus of the atoms, while the electrons are found in the planetary system revolving in orbits about the nucleus. The electrons in the outer orbit of the planetary system determine the valence of the element and thus are most important in our study of chemistry.

The number of electrons in the planetary system of the atom has been determined experimentally. This is called the atomic number of the element. Since the atom is neutral, the number of free protons (in the nucleus) is equal to the atomic number. The exact atomic weight of the individual atoms can also be found by experiment. This weight represents the number of protons and neutrons in the atom. The number of neutrons is found by subtracting from the atomic weight, the number of protons as determined from the atomic number. Further experiments have made it possible for scientists to decide on the arrangement of the electrons in the orbits of the atoms, though little is known of the arrangement of the neutrons and protons in the nuclei. The diagrams in Chapter VII show the structure of a few of the atoms. Table XIV outlines the results of these experiments on atomic structure, listing the elements in the order of their atomic number.

As indicated in the previous paragraph, Table XIV shows that the number of protons is equal to the total number of electrons in the atom, and that the sum of the number of neutrons and protons is equal to the atomic weight of the element. Moreover, all of the rare gases have complete orbits of eight electrons (except helium with two). Note also that with each succeeding element, the extra electron is added according to a definite arrangement.

TABLE XIV

ARRANGEMENT OF ELECTRONS IN THE ORBITS OF ATOMS

<i>Element</i>	<i>At.</i> <i>No.</i>	<i>Orbits</i> <i>1 2 3 4 5 6 7</i>							<i>Element</i>	<i>At.</i> <i>No.</i>	<i>Orbits</i> <i>1 2 3 4 5 6 7</i>						
Hydrogen	1	1							Yttrium	39	2	8	18	9	2		
Helium	2	2							Zirconium	40	2	8	18	10	2		
Lithium	3	2	1						Columbium	41	2	8	18	11	2		
Beryllium	4	2	2						Molybdenum	42	2	8	18	12	2		
Boron	5	2	3						Masurium	43	2	8	18	13	2		
Carbon	6	2	4						Ruthenium	44	2	8	18	14	2		
Nitrogen	7	2	5						Rhodium	45	2	8	18	15	2		
Oxygen	8	2	6						Palladium	46	2	8	18	18			
Fluorine	9	2	7						Silver	47	2	8	18	18	1		
Neon	10	2	8						Cadmium	48	2	8	18	18	2		
Sodium	11	2	8	1					Indium	49	2	8	18	18	3		
Magnesium	12	2	8	2					Tin	50	2	8	18	18	4		
Aluminium	13	2	8	3					Antimony	51	2	8	18	18	5		
Silicon	14	2	8	4					Tellurium	52	2	8	18	18	6		
Phosphorus	15	2	8	5					Iodine	53	2	8	18	18	7		
Sulphur	16	2	8	6					Xenon	54	2	8	18	18	8		
Chlorine	17	2	8	7					Caesium	55	2	8	18	18	8	1	
Argon	18	2	8	8					Barium	56	2	8	18	18	8	2	
Potassium	19	2	8	8	1				Lanthanum	57	2	8	18	18	9	2	
Calcium	20	2	8	8	2				Cerium	58	2	8	18	19	9	2	
Scandium	21	2	8	9	2				Praseodym-								
Titanium	22	2	8	10	2				ium	59	2	8	18	20	9	2	
Vanadium	23	2	8	11	2				Neodymium	60	2	8	18	21	9	2	
Chromium	24	2	8	13	1				Illinium	61	2	8	18	22	9	2	
Manganese	25	2	8	13	2				Samarium	62	2	8	18	23	9	2	
Iron	26	2	8	14	2				Europium	63	2	8	18	24	9	2	
Cobalt	27	2	8	15	2				Gadolinium	64	2	8	18	25	9	2	
Nickel	28	2	8	16	2				Terbium	65	2	8	18	26	9	2	
Copper	29	2	8	18	1				Dysprosium	66	2	8	18	27	9	2	
Zinc	30	2	8	18	2				Holmium	67	2	8	18	28	9	2	
Gallium	31	2	8	18	3				Erbium	68	2	8	18	29	9	2	
Germanium	32	2	8	18	4				Thulium	69	2	8	18	30	9	2	
Arsenic	33	2	8	18	5				Ytterbium	70	2	8	18	31	9	2	
Selenium	34	2	8	18	6				Lutecium	71	2	8	18	32	9	2	
Bromine	35	2	8	18	7				Hafnium	72	2	8	18	32	10	2	
Krypton	36	2	8	18	8				Tantalum	73	2	8	18	32	11	2	
Rubidium	37	2	8	18	8	1			Tungsten	74	2	8	18	32	12	2	
Strontium	38	2	8	18	8	2			Rhenium	75	2	8	18	32	13	2	

TABLE XIV (Continued)

<i>At.</i> <i>Orbits</i>								<i>At.</i> <i>Orbits</i>									
<i>Element</i>	<i>No.</i>	1	2	3	4	5	6	7	<i>Element</i>	<i>No.</i>	1	2	3	4	5	6	7
Osmium	76	2	8	18	32	14	2		Alabamine	85	2	8	18	32	18	7	
Iridium	77	2	8	18	32	15	2		Radon	86	2	8	18	32	18	8	
Platinum	78	2	8	18	32	16	2		Virginium	87	2	8	18	32	18	8	1
Gold	79	2	8	18	32	18	1		Radium	88	2	8	18	32	18	8	2
Mercury	80	2	8	18	32	18	2		Actinium	89	2	8	18	32	18	9	2
Thallium	81	2	8	18	32	18	3		Thorium	90	2	8	18	32	18	10	2
Lead	82	2	8	18	32	18	4		Protoactinium	91	2	8	18	32	18	11	2
Bismuth	83	2	8	18	32	18	5		Uranium	92	2	8	18	32	18	12	2
Polonium	84	2	8	18	32	18	6										

Isotopes. — A method has been devised by Aston to determine the exact atomic weight of individual atoms. Using this method, some elements were found to have atoms with different weights. For example, some chlorine atoms have an atomic weight of 35,

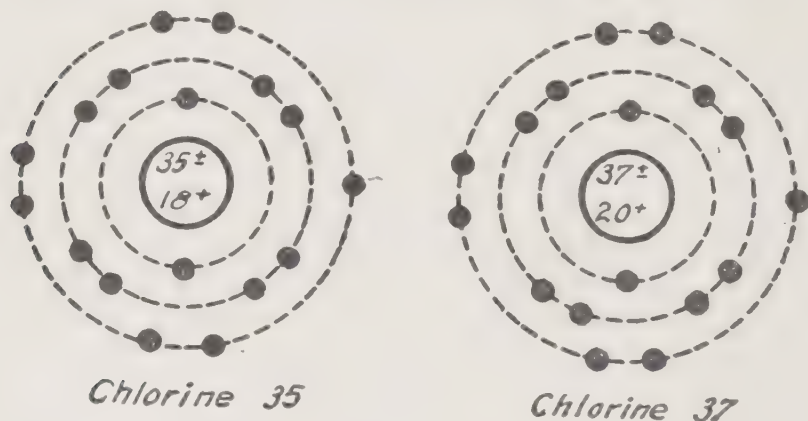


FIG. 32. Isotopes of Chlorine

and others weigh 37 (Fig. 32). These are known as **isotopes of chlorine**. Their existence has also been demonstrated by the method of combining weights (Chapter IX), from which the atomic weight of chlorine is found to be a fractional weight,

35.457. This fractional weight would be impossible with all the atoms alike, since there is no evidence of fractional protons or neutrons. Moreover, accurate experiments have been made on the diffusion of chlorine through a membrane, in which it was shown that the chlorine which diffused was slightly lighter in weight than the part which did not pass through the membrane. Recent experiments have shown that many elements have isotopes. The two or more atoms, known as isotopes of an element, have different atomic weights but the same atomic number. In other words, there is a different number of neutrons in the nucleus, while the number of protons in the nucleus and the number and arrangement of electrons in the planetary system are alike in all the iso-



FIG. 33. Isotopes of Hydrogen

topes of an element (Figs. 32, 33). The difference in the structure of the nucleus has little effect on the chemical properties of the element, since it is the atomic number and especially the electrons in the outer orbit of an atom, that gives an element its characteristic properties.

Deuterium. — The most interesting isotope is the atom of hydrogen with atomic weight of two. As we have learned, the nucleus of most hydrogen atoms consists of one proton. There is an isotope of hydrogen, however, whose nucleus consists of one proton and one neutron (Fig. 33). While the addition of one or more neutrons to an atom that weighs as much as chlorine makes a comparatively small change in weight, the addition of one neutron

to a hydrogen atom doubles the weight. As a result the isotope of hydrogen differs materially from ordinary hydrogen and has been designated by the special name, **deuterium**. Water in which deuterium is substituted for ordinary hydrogen is designated as **deuterium oxide or heavy water**.

In water, as it occurs in nature, approximately one part in 5,000 is deuterium oxide. When water undergoes electrolysis or is distilled, the heavier deuterium oxide molecules do not change so easily. In this way, by continuous electrolysis or distillation, pure deuterium oxide or heavy water can be prepared. This is very expensive and of interest at present only for experimental work.

Compounds can be formed from heavy water similar to those made with ordinary water. Heavy water seems to be harmful to most forms of life.

THE PERIODIC TABLE

The relationship between the atomic structure and properties of elements has been demonstrated repeatedly in this and previous chapters. In 1869, however, long before scientists had any conception of protons and electrons, Mendeléeff, a Russian chemist and teacher, discovered a relationship between the properties of elements and their atomic weights that is of inestimable value to-day. It is said that Mendeléeff was intent upon a method of making it easier for his students to remember the properties of the elements. On a series of cards he wrote the names of the elements with their characteristic properties. He pinned these cards to the wall with the elements having similar properties grouped together. As he studied these cards, he realized that there was a surprisingly close periodic relationship between the atomic weights of the elements and their other properties. The result of this observation, together with Mendeléeff's knowledge of the suggestions of earlier scientists regarding such similarity in the properties of the elements, led him to arrange the elements then known into a table called the **periodic table**. While this arrangement of elements was at first not generally accepted by chemists, later studies proved it to be so convincing that the work became the foundation of much research and of many important dis-

coveries. Since Mendeléeff's time the study of atomic structure has further explained the periodic arrangement of the elements.

The Periodic Arrangement of the Elements. — The relationship between the atomic weights and properties of the elements, as noted by Mendeléeff, is illustrated by the arrangement of the eighteen elements in Table XV.

It is interesting to study the properties of the elements of a **series**, as the horizontal rows are called. Beginning the second series, lithium is an active metal. The metallic properties of the elements of this series decrease from lithium to fluorine, the most reactive non-metal. After fluorine, neon is the next element in the order of atomic weight. It is like helium, which is above it in the table, in being an inert, inactive gas. Sodium, the next element in order of atomic weight, is placed below lithium, and thus another series is started in which the properties of the elements vary just as in the series above it, from the active metal sodium to the active non-metal chlorine. Each element in the third series is directly below an element it resembles in the second series. That is, there exists a similarity in properties between the following **groups** of elements — sodium and lithium, magnesium and beryllium, aluminium and boron, silicon and carbon, phosphorus and nitrogen, sulphur and oxygen, chlorine and fluorine. Argon, an inert, inactive gas like neon and helium, completes the series. This similarity may be extended throughout all the elements of the periodic table (Table XVI). Many periodic tables divide Groups I to VII into two **families** which differ from each other in properties. Thus in Group I, the family to the left consists of lithium, sodium, potassium, rubidium, and caesium, while the other family consists of copper, silver, and gold. Practically all the succeeding chapters deal with families of elements as represented in the periodic table.

Although this table as suggested by Mendeléeff is not perfect, elements that fall in the same group are surprisingly similar in properties. Moreover, many properties change gradually from one element to another in the group. This will be noted in the study of several families of elements in the following chapters.

TABLE XV
PERIODIC RELATIONSHIP OF THE ELEMENTS OF THREE SERIES
(Hydrogen to chlorine, inclusive)

	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group 0
Series I	(1) Hydrogen							(2) Helium: gas; inert, inactive; valence 0
	(3) Lithium: soft metal; very re-active;	(4) Beryllium: metal, reactive;	(5) Boron: non-metal;	(6) Carbon: non-metal;	(7) Nitrogen: non-metal;	(8) Oxygen: non-metal; reacts (high temp.);	(9) Fluorine: non-metal; very re-active, poisonous; valence -1	(10) Neon: gas; inert, active; valence 0
Series II	valence +1	valence +2	valence +3	valence +4, -4	valence +5, -3	valence -2		
	(11) Sodium: soft metal; very re-active;	(12) Magnesium: metal; reactive;	(13) Aluminum: metal and non-metal;	(14) Silicon: non-metal;	(15) Phosphorus: non-metal;	(16) Sulphur: non-metal; reacts (high temp.);	(17) Chlorine: non-metal; reactive, poisonous; valence +7, -1	(18) Argon: gas; inert, active; valence 0
Series III	valence +1	valence +2	valence +3	valence +4, -4	valence +5, -3	valence +6, -2		

The relationship between the properties of elements and their atomic weights is undeniable, but at first it seemed unreasonable to scientists because it could not be explained. Not until the atomic number and its meaning were discovered did scientists understand this relationship. It was then found that the atomic numbers and the atomic weights of the elements increased in the same order, and the atomic number became the basis for the periodic arrangement of the elements.

The relationship between the structure of the atom and an arrangement of elements according to atomic number and atomic weight is illustrated in the diagrams of Table XVII.¹ The elements are placed in the same order as in the periodic table. The diagrams show that this arrangement corresponds to the number of electrons in the planetary system of the atom, which is the atomic number. For example hydrogen, atomic number 1 with one electron in the planetary system, is followed by helium, atomic number 2 with two electrons in the planetary system, and then by lithium, atomic number 3 with three electrons in two orbits of the planetary system (Table XIV). It follows that we may think of the periodic table as an arrangement of the elements in the order of their atomic number, a more nearly exact and fundamental property than the atomic weight.

It is interesting to note that scientists found three pairs of elements which did not fit into the periodic table in the exact order of their atomic weights. Tellurium and iodine, for example, could be placed in groups with similar properties only by transposing them. Scientists supposed that some time it could be shown that one of the weights was incorrect, thus justifying the exchange of places. Recent determinations of the atomic number, however, indicate that these elements are in the correct order according to this property. The other pairs of transposed elements, argon and potassium, and cobalt and nickel, are in the correct order according to the atomic number. This again demonstrates that the atomic number, instead of the atomic weight, is the more fundamental property as a basis for the classification of the elements.

¹ This arrangement of diagrams was suggested to the authors by the article "The Structure of Matter," by Otto Reinmuth, *Jour. Chem. Ed.*, 5, 1312.

















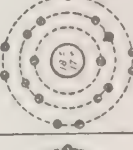
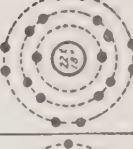
TABLE XVI
PERIODIC ARRANGEMENT OF THE ELEMENTS

Series no.	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group 0	Group VIII		
1	1 H 1.0080							2 He 4.002			
2	3 Li 6.940	4 Be 9.02	5 B 10.82	6 C 12.01	7 N 14.008	8 O 16.000	9 F 19.00	10 Ne 20.183			
3	11 Na 22.997	12 Mg 24.32	13 Al 26.97	14 Si 28.06	15 P 30.98	16 S 32.06	17 Cl 35.457	18 Ar 39.944			
4	19 K 39.096	20 Ca 40.08	21 Sc 45.10	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.93	26 Fe 55.85	27 Co 58.94	28 Ni 58.69	
	29 Cu 63.57	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.91	34 Se 78.96	35 Br 79.916	36 Kr 83.7			

5	37 Rb 85.48	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Cb 92.91	42 Mo 95.95	43 Ma	44 Ru 101.7	45 Rh 102.91	46 Pd 106.7
	47 Ag 107.88	48 Cd 112.41	49 In 114.76	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.92	54 Xe 131.3		
6	55 Cs 132.91	56 Ba 137.36	57-71 Rare earths	72 Hf 178.6	73 Ta 180.88	74 W 183.92	75 Re 186.31	76 Os 190.2	77 Ir 193.1	78 Pt 195.23
	79 Au 197.2	80 Hg 200.61	81 Tl 204.39	82 Pb 207.21	83 Bi 209.00	84 Po	85 *	86 Rn 222		
7	87 *	88 Ra 226.05	89 Ac	90 Th 232.12	91 Pa	92 U 238.07				

* Element 85, alabamine, and element 87, virginium, have been reported.

TABLE XVII
STRUCTURE OF ATOMS

Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8
1 <i>H</i> 							2 <i>He</i> 
1.0081							4.002
3 <i>Li</i> 	4 <i>Be</i> 	5 <i>B</i> 	6 <i>C</i> 	7 <i>N</i> 	8 <i>O</i> 	9 <i>F</i> 	10 <i>Ne</i> 
6.940	9.02	10.82	12.010	14.008	16	19	20.183
11 <i>Na</i> 	12 <i>Mg</i> 	13 <i>Al</i> 	14 <i>Si</i> 	15 <i>P</i> 	16 <i>S</i> 	17 <i>Cl</i> 	18 <i>A</i> 
22.997	24.32	26.97	28.06	30.98	32.06	35.457	39.944

Use of the Periodic Table in the Study of Chemistry. — From the previous discussion it is evident that the periodic table will enable us to study the elements in groups rather than individually. We may determine also many properties of an element before studying about it, by referring to its position in the periodic table. A few rules to aid in this study are as follows:

1. *Positive Valence.* In Groups I to VII the usual positive valence of an element is the same as the group number.² This means that an element in Group I has a positive valence of one. In a similar way the positive valence of elements in the other groups corresponds to the group number. It is with this positive valence that elements combine with oxygen, chlorine, sulphur, and the radicals: hydroxide, nitrate, and sulphate. Thus the formulas for the oxides of the elements of Series 3 are as follows:



From a study of the arrangement of electrons in orbits shown in Table XIV, it is evident that the number of electrons in the outer orbit of the planetary system (which determines the valence) often corresponds to the group number. Thus lithium and sodium, in Group I, have one electron in their outer orbits or a valence of positive one, while fluorine and chlorine, in Group VII, have seven electrons in their outer orbits, making a valence of positive seven (Chapter VII).

2. *Negative Valence.* The elements in Groups IV to VII with four to seven electrons in their outer orbits show negative valences also. The elements of Group IV have valences of positive four and negative four; those in Group V have valences of positive five and negative three; those in Group VI have valences of positive six and negative two; and those in Group VII have valences of positive seven and negative one. It is with the negative valence that elements combine with hydrogen and the metals. Thus the formulas for the hydrogen compounds of the elements of Series 3 are as follows:



² Certain metals have more than one positive valence. These will be indicated in later chapters as occasion arises. We have already learned that copper

3. *Base-Forming and Acid-Forming Properties.* Base-forming elements are metals, acid-forming elements are non-metals; typical examples of metals are caesium, potassium, and sodium (Group I) whose hydroxides are strong bases; and examples of non-metals are sulphur and chlorine (Groups VI and VII) whose hydroxides are acids. Besides metals and non-metals, there are several elements the oxides and hydroxides of which act as though they were both acid-forming and base-forming. Such compounds are called **amphoteric**. The relationship between the anhydride, the hydroxide, and the ions formed by each hydroxide for a series of elements is shown in Table XVIII.

TABLE XVIII

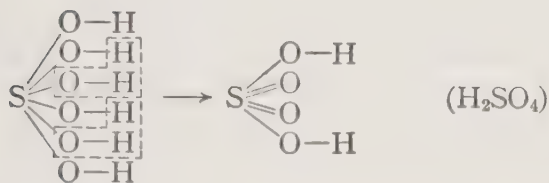
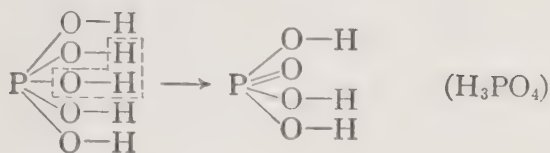
ACID-FORMING, BASE-FORMING, AMPHOTERIC PROPERTIES

<i>Anhydride</i>	<i>Hydroxide</i>	<i>Ions Formed</i>
Na ₂ O	NaOH	Na ⁺ , OH ⁻
MgO	Mg(OH) ₂	Mg ⁺⁺ , 2OH ⁻
Al ₂ O ₃	Al(OH) ₃ (H ₃ AlO ₃)	Al ⁺⁺⁺ , 3OH ⁻ 3H ⁺ , AlO ₃ ⁼
SiO ₂	Si(OH) ₄ (H ₄ SiO ₄)	4H ⁺ , SiO ₄ ⁼
P ₂ O ₅	P(OH) ₅ (H ₅ PO ₅)	3H ⁺ , PO ₄ ⁼
SO ₃	S(OH) ₆ (H ₆ SO ₆)	2H ⁺ , SO ₄ ⁼
Cl ₂ O ₇	Cl(OH) ₇ (H ₇ ClO ₇)	H ⁺ , ClO ₄ ⁼

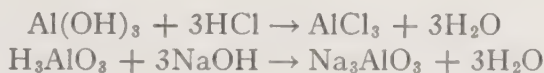
It is shown in Table XVIII that the elements of a series in the periodic table become more acidic as we pass from left to right; sodium hydroxide is a strong base, magnesium hydroxide a mild base (milk of magnesia), aluminium hydroxide is amphoteric and acts as a base and as an acid, while the hydroxides of silicon, phosphorus, sulphur, and chlorine are increasingly acidic. The hydroxide of a non-metal does not always look familiar as an acid,

(Group I) has a valence of positive two, although it forms some compounds in which the valence is positive one.

because the hydroxide may give up one or more molecules of water as shown by the formulas:



As indicated in Table XVIII, an amphoteric hydroxide, such as aluminium hydroxide, ionizes as a weak base and a weak acid; in other words, it is a base when reacting with an acid and it is an acid when reacting with a strong base. This is shown by the equations:



The position of an element in the periodic table suggests the typical acid-forming, base-forming, and amphoteric properties. In a series, reading from left to right, the base-forming properties decrease, and amphoteric, then acid-forming properties appear (Table XVIII); in a group, reading from top to bottom, the elements become increasingly base-forming (or decreasingly acid-forming). If any elements of a group are acid-forming, they are at the top of the group (IV, V, VI, and VII) and the amphoteric and base-forming elements are below them. In any group, the elements in the family to the left have a tendency to be base-forming (or less acid-forming) while those of the family to the right are acid-forming (or less base-forming); for example, caesium of Group I (not gold) is the strongest base-forming element, while

fluorine and chlorine of Group VII are strongly acid-forming elements.

Value of the Periodic Table to Scientists. — When Mendeléeff arranged the elements in this periodic table, there were many blank spaces to be filled. From the properties of the elements that were near these blank spaces, Mendeléeff predicted the properties of the elements that were to be discovered. Immediately scientists throughout the world began to search for the new elements. One by one discoveries have been made, until at present we believe that elements to fill all the blank spaces in the periodic table have been reported. The periodic table has been of inestimable value in research. It has given a basis for the development of research on atomic weights and other properties of the elements, and a means of showing the coördination of results.

QUESTIONS AND PROBLEMS

1. What are the contributions of Dalton (Chapter VII) and Mendeléeff to the chemistry of the periodic table, and the approximate date at which each did his work?
2. Name the element in Series 3, Group VI; the two elements of Series 4, Group I, and tell which element is more strongly base-forming.
3. Compare the properties of the elements with atomic numbers 85 and 35; the elements with atomic numbers 87 and 55.
4. What is the name and symbol of the element with atomic weight 209; the element that has 10 neutrons and 9 protons in its nucleus?
5. Diagram the atoms of sulphur and of chlorine. Use the diagrams to explain the characteristic valences of each element.
6. Using the diagrams of the atoms, show why lithium and sodium have the same valence. Why should nitrogen and phosphorus have the same valences? What valences have they?
7. Using the characteristic valence obtained from the periodic table, write the formulas for the hydrides and the oxides of arsenic (33), tellurium (52), and silicon (14).
8. Using the valences indicated by the periodic table, write formulas for the hydroxides of rubidium (37), bromine (35), sulphur (16), aluminium (13), and nitrogen (7). Write the formula for the characteristic acid of the hydroxides that are acidic or amphoteric. Arrange the hydroxides in the order: strongest acid to strongest base.
9. Show the valence of the elements of Group V, nitrogen family, by writing formulas for the hydride and the oxide of each element.

10. Show by writing ionization equations whether the following hydroxides are acidic or basic: $\text{Cl}(\text{OH})_6$; $\text{Mg}(\text{OH})_2$.
11. Write equations to show how aluminium hydroxide ionizes as a base and as an acid; write equations to show the reaction of aluminium hydroxide with sulphuric acid, and with potassium hydroxide. Name the salts formed.
12. Explain the meaning of the term—*isotope*. Diagram the isotopes of chlorine and explain the structure of each isotope.
13. Indicate the valence of each atom in the following formulas. Is it the valence indicated in the periodic table? K_2SO_4 ; AuCl_3 ; KClO_3 ; $\text{K}_2\text{Cr}_2\text{O}_7$; $\text{H}_4\text{P}_2\text{O}_7$; CCl_4 ; MnO_2 ; Mn_2O_7 ; KMnO_4 ; Na_2SO_3 ; $\text{Cu}(\text{NO}_3)_2$; CrO_3 ; CrCl_3 ; HVO_3 .
14. Write equations which show the amphoteric properties of antimonious hydroxide $\text{Sb}(\text{OH})_3$.
15. Using the valence indicated by the periodic table, write formulas and names of compounds formed when (1) silver combines with arsenic, (2) zinc combines with selenium, (3) caesium combines with bromine, (4) germanium combines with sulphur, (5) sodium combines with tellurium, (6) tin combines with chlorine, (7) hydrogen combines with phosphorus, (8) manganese combines with oxygen.
16. Arrange the following elements in the order of strongest base-forming to strongest acid-forming: P, Mg, Sb, Cs, Ca, F, N, Cl.
17. What element has the strongest base-forming property; the strongest acid-forming property?

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CHAPTER XXII

THE CHLORINE FAMILY

Introduction. — The chlorine family of Group VII in the periodic table consists of four elements, so similar in properties that they may be studied together. These elements — fluorine, chlorine, bromine, and iodine — are called the chlorine family because chlorine is far more abundant and familiar than the other three elements. Another name also given to this group of elements is the halogen family. The term **halogen** is derived from Greek words meaning "salt-forming," because all the elements combine with metals to form stable salts, similar to sodium chloride, NaCl . In addition to the elements mentioned, the periodic table indicates that the element with atomic number 85 also belongs to this family. F. Allison and co-workers, at Alabama Polytechnic Institute, have reported (1931) traces of element 85 in several substances of nature, such as sea-water, fluorite, CaF_2 , monazite sand, and potassium bromide. The new element (85) was named alabamine.

Occurrence. — Since the halogens are chemically reactive, they are never found free in nature. Chlorine, bromine, and iodine combine easily with metals to form halides, such as calcium chloride, CaCl_2 , potassium bromide, KBr , and sodium iodide, NaI . These compounds are soluble in water, and through the ages the rivers have dissolved them and carried them to the seas. To-day the halogens are obtained commercially from deposits left by the evaporation of water containing the salts. The great nitrate beds of Chile contain sodium nitrate mixed with sodium iodate, from which iodine is obtained. Compounds of iodine constitute about 2 per cent of the ash of seaweeds and are present in traces in most marine fishes. Sodium chloride with traces of sodium bromide is mined in several parts of the world. The fluo-

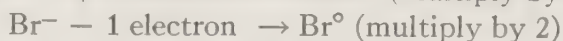
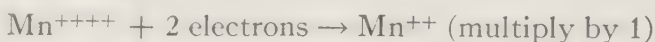
rine compounds in nature are less soluble than the other halides and occur as minerals in widely distributed places. Fluorspar, CaF_2 , and cryolite, Na_3AlF_6 , are the most abundant of these minerals. Fluorine compounds are found in the teeth and bones of animals.

Preparation of the Elements. — Fluorine is such an active element and its compounds are so stable that, although its occurrence in fluorspar was demonstrated in 1811, the gaseous element was not prepared successfully until 1886. It was then prepared by electrolysis of liquid hydrogen fluoride, using potassium acid fluoride, KHF_2 , as the electrolyte.

Chlorine, bromine, and iodine each may be prepared by the reaction of the corresponding halide with manganese dioxide and sulphuric acid. The equation for the preparation of bromine follows:

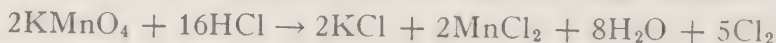


The reaction is of the oxidation-reduction type, as is shown by the electron change:



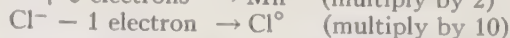
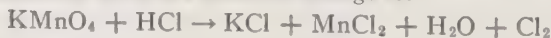
Similar equations may be written for the preparation of chlorine from sodium chloride and of iodine from sodium iodide.

A convenient, though more expensive, method for the preparation of chlorine is illustrated by the oxidation of hydrochloric acid with potassium permanganate. It is a method often used when small quantities of chlorine are needed, such as in lecture demonstration. The equation for the reaction is as follows:¹



Commercially, chlorine gas is prepared by the electrolysis of

¹ It may be helpful to explain the method of balancing this type of reaction. The skeleton equation with the electron change is:



It follows that two molecules of potassium permanganate act as an oxidizing agent with ten molecules of hydrochloric acid. However, the compounds

sodium chloride solution. The Nelson cell (Fig. 34) is designed to separate the products of electrolysis, namely, chlorine gas and sodium hydroxide, during the reaction. A direct current is passed through a concentrated solution of sodium chloride (C) causing the chloride ions to collect at the anode A and the sodium ions to collect at the cathode B. At the carbon anode, the chloride ion gives up its electron and becomes a chlorine atom. The chlorine atoms, in turn, become chlorine molecules, which are evolved as chlorine gas at the outlet E. The cathode is a perforated metal diaphragm lined with asbestos. Sodium ions pass through the asbestos to the cathode, where they take on an electron and become sodium atoms. Immediately the element sodium reacts with the water as follows:

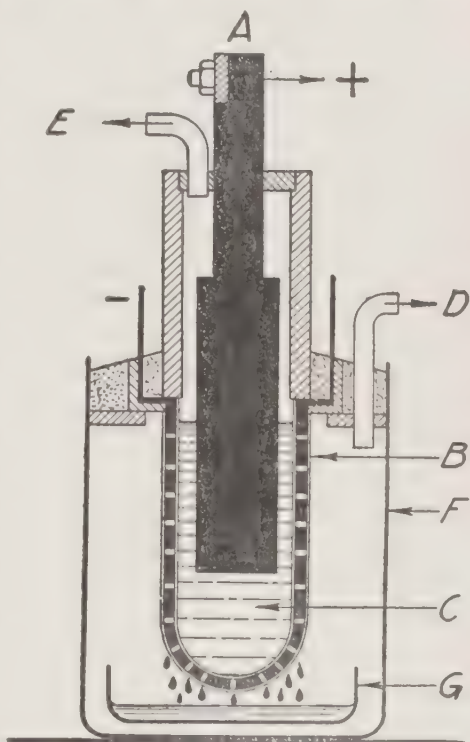
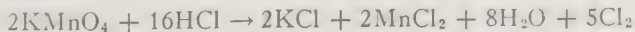


FIG. 34. The Nelson Cell



The sodium hydroxide drips into the vessel G, and hydrogen gas escapes at the outlet D. Except for this ingenious method of separating the products of electrolysis, the chlorine gas would react with the sodium hydroxide. The electrolysis of sodium chloride in the Nelson cell prepares three important commercial products. Potassium chloride and manganous chloride require chlorine, which must be furnished by additional molecules of hydrochloric acid. In all, sixteen molecules of hydrochloric acid are necessary to balance the equation. The balanced equation reads:



products, chlorine gas, hydrogen gas, and sodium hydroxide (lye). An equation which represents the process of electrolysis is the following:



There are brine deposits and mineral springs from which we obtain halogen salts — sodium chloride, sodium bromide, and magnesium bromide; such deposits are located in Michigan and Ohio. After the sodium chloride has been crystallized from the brine, the resulting liquor is subjected to a process of electrolysis in which the element bromine is recovered. Sea-water is another source of bromine; it contains only about sixty-seven parts of bromine per million parts of water, but this is sufficient for commercial recovery of the bromine. The method of displacement is used to obtain bromine from sea-water, as shown by the equation:



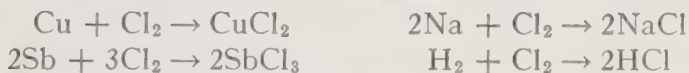
Properties of the Halogen Elements. — The characteristic physical and chemical properties of the four elements are shown in Table XIX.

TABLE XIX

PROPERTIES OF THE ELEMENTS OF THE HALOGEN FAMILY

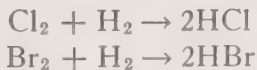
<i>Property</i>	<i>Fluorine</i>	<i>Chlorine</i>	<i>Bromine</i>	<i>Iodine</i>
Atomic weight	19	35.457	79.916	126.93
Physical state	gas	gas	liquid	solid
Color	pale yellow	yellow	brown	purple (gas)
Boiling-point	−187°	−34°	59°	184°
Melting-point	−223°	−102°	−7°	114°
Activity	very active	reactive	reactive	least active
with water	soluble and reacts	soluble and reacts slowly	soluble	slightly soluble
with hydrogen	unites explosively	unites by aid of sunlight	unites by aid of heat and a catalyst	unites by aid of heat and a catalyst
displacement	displaces Cl, Br, I from compounds	displaces Br, I from compounds	displaces I from compounds	

It will be noted that the physical properties of the halogens change gradually as the atomic weight increases; that is, from fluorine, a gas, to iodine, a solid, the density increases, the color becomes darker, the boiling-point becomes higher, and the solubility in water decreases. In a similar manner the chemical properties vary with increase in atomic weight. From its position in the periodic table, it is evident that fluorine is the most reactive non-metal, having the greatest tendency to attract an electron and become negative. Chlorine is also very reactive and at ordinary temperature unites with many elements. Some of these reactions are shown by the following equations:



Bromine and iodine undergo these same direct union reactions, but less readily.

Other important reactions of the elements indicate that fluorine and chlorine are, in order, more reactive than bromine and iodine. By mere contact of fluorine with moist hydrogen, an explosive reaction occurs, forming hydrogen fluoride, while chlorine gas is active enough to combine with hydrogen when the mixture is placed in the sunlight. The conditions necessary for the direct union reaction of hydrogen with the element is an indication of the reactivity of the halogen. Bromine and iodine also combine with hydrogen, but because the elements are less active than the other halogens, the reaction requires the aid of a catalyst. Typical direct union reactions are:



The order of reactivity of the halogens is shown in another series of reactions, of the displacement type. The halogen elements are oxidizing agents and hence have a tendency to take electrons from other elements. According to the ease with which they acquire electrons, the four halogens make the following displacement series: fluorine, chlorine, bromine, and iodine (compare with electrochemical series of metals, Chapter XIV). In the reac-

tion of a halogen with a salt, fluorine (the most reactive) will displace chlorine from a chloride, bromine from a bromide, and iodine from an iodide; chlorine (quite reactive) will displace bromine from a bromide and iodine from an iodide; and bromine is active enough to displace iodine from an iodide. Typical displacement reactions are:



The Hydrogen Halides. — The formation of a hydride by direct union of the halogen and hydrogen was mentioned in Table XIX. The hydrides are hydrogen fluoride, HF, hydrogen chloride, HCl, hydrogen bromide, HBr, and hydrogen iodide, HI. They are colorless gases with a penetrating odor. The hydrides are soluble in water, and form acids. The formulas and names for these acids are as follows:

hydrofluoric
hydrobromic

HF
HBr

hydrochloric
hydriodic

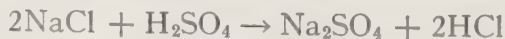
HCl
HI

Hydrogen fluoride gas is made by the following reaction:



The water solution of the gas is hydrofluoric acid. The gas, as well as hydrofluoric acid, will dissolve glass. When glass is exposed to hydrogen fluoride gas, the surface is marked or etched; this is a method used to make the designs on etched glass dishes and the marks indicating divisions on glass graduates, burettes, and other apparatus. It is evident that hydrofluoric acid cannot be kept in a glass bottle. Bottles made of wax or paraffin are commonly used.

Hydrogen chloride gas is made by the following reaction:



Hydrogen chloride, a colorless gas, is so soluble in water that when liberated it dissolves in the moisture of the air, forming tiny droplets and giving a fog of hydrochloric acid. An apparatus

showing the marked solubility of hydrogen chloride gas is illustrated in Figure 35. The flask A is filled with hydrogen chloride gas and is connected by a glass tube to a beaker filled with water. A medicine dropper B may be inserted in the stopper of the flask. This affords a means of forcing a few drops of water into the flask A. The water dissolves sufficient hydrogen chloride gas to create a partial vacuum in the flask A. Then the pressure of the atmosphere on the surface of the water in the beaker causes water to rush through the tube into the flask A, giving the effect of a fountain.

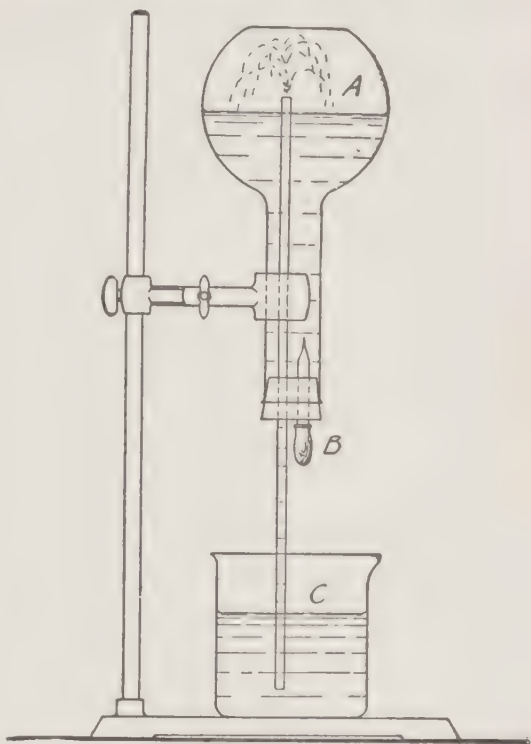


FIG. 35. Apparatus to Show the Solubility of Hydrogen Chloride

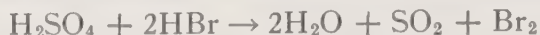
Hydrogen chloride gas and ammonia gas unite in a way that gives visible evidence of the chemical change. Ammonium chloride is formed as a dense white cloud of solid particles. The equation for the reaction is as follows:



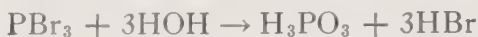
The water solution of hydrogen chloride gas is hydrochloric acid, one of the most familiar and useful acids in the laboratory. It is a strong acid and shows all the properties characteristic of acids; for example, it is an electrolyte, it has a sour taste, it affects indicators, it reacts with certain metals to evolve hydrogen gas, and it reacts with oxides of metals and with bases. Since it is not

an oxidizing agent, it cannot react with metals below hydrogen in the electrochemical series in the same way that nitric and sulphuric acids react.

Hydrogen bromide and hydrogen iodide are unstable gases and are easily oxidized to form the elements bromine and iodine. Sulphuric acid oxidizes hydrogen bromide according to the equation:



A similar reaction occurs with hydrogen iodide. It follows that it would not be practical to use the reaction of a salt with sulphuric acid for the preparation of hydrogen bromide or hydrogen iodide. However, the hydrolysis of phosphorus tribromide and of phosphorus triiodide gives a convenient means of obtaining the compounds. The reactions are as follows:

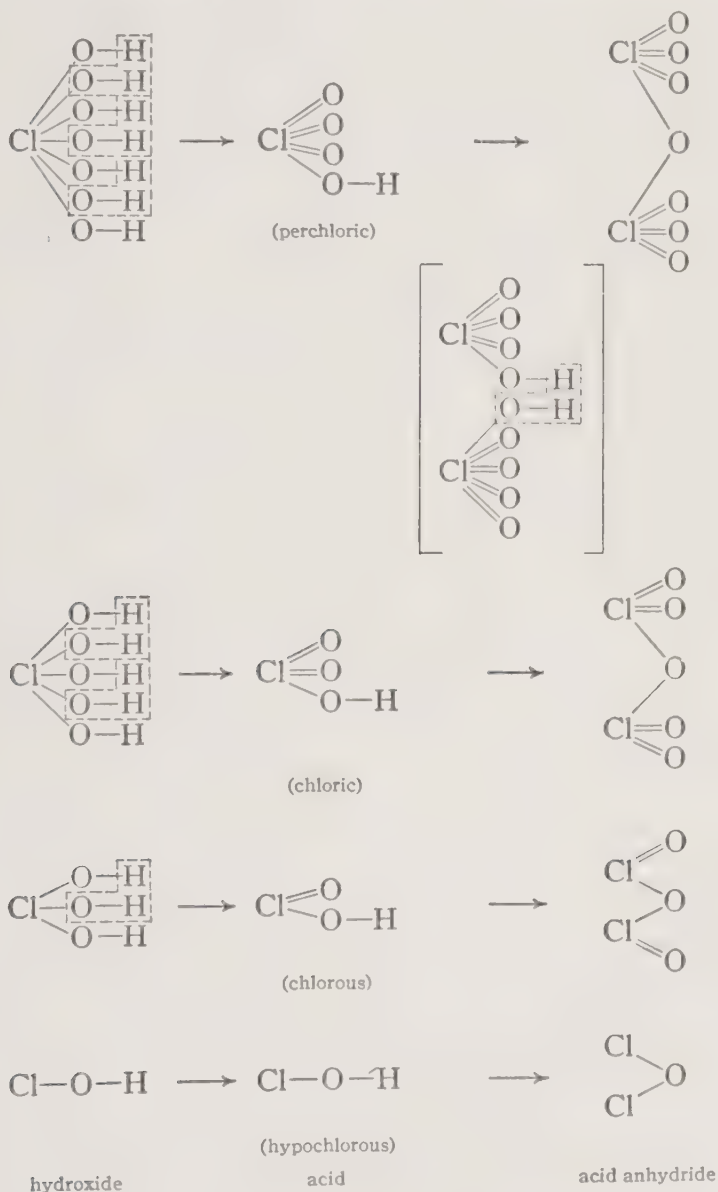


Nomenclature of the Halogen Compounds. — It will be recalled (Chapter X) that the classification of acids so far studied is (1) those having names ending in *-ic*, (2) those having names ending in *-ous*, and (3) binary acids. The chlorine series of acids calls for an addition to this nomenclature. When an acid contains less oxygen than the *-ous* acid, it is named by using the prefix **hypo-** as in **hypochlorous** acid. When an acid contains more oxygen than the *-ic* acid, it is named by using the prefix **per-** as in **perchloric** acid. The salts of these acids are named in the usual manner. The following acids and salts represent the entire chlorine series:

HCl	hydrochloric	NaCl	sodium chloride
HClO	hypochlorous	NaClO	sodium hypochlorite
HClO ₂	chlorous	NaClO ₂	sodium chlorite
HClO ₃	chloric	NaClO ₃	sodium chlorate
HClO ₄	perchloric	NaClO ₄	sodium perchlorate

Compounds are known in which bromine or iodine is substituted for chlorine in most of these formulas, with a corresponding change in the name of the compound; for example, HBrO is hypobromous acid, HIO₃ is iodic acid, NaBrO is sodium hypobromite, and NaIO₃ is sodium iodate.

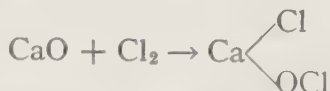
As shown in Chapter XXI, acids are essentially the hydroxides of non-metals. The relationship of the acid to the hydroxide and to the acid anhydride is shown by the following graphic formulas:



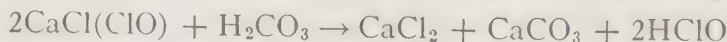
The Halogens in Daily Life. — We meet the halogens in daily life more frequently than we are aware of them. Meals without salt would not only be tasteless, but would deprive us of two elements essential to life. The chloride ion is of especial importance for the production of hydrochloric acid in the stomach. We are not so careful of the inclusion of iodide ion as iodized salt or as a component of sea food or drinking water, although it is a well-known fact that a trace of iodine compounds is necessary for complete nutrition. In some localities, well-water contains fluorides; if the water is used for drinking purposes, it may cause brown spots or "mottled enamel" on the teeth. Bromide salts are used as sedatives.

Tincture of iodine, which is iodine dissolved in alcohol, is used as an antiseptic because of its toxic effect on bacteria. Its extensive use on open cuts is discouraged, as there is some harmful effect on the body tissues.

Chlorine is known as an active oxidizing agent. This property makes it valuable in the purification of water either for drinking purposes or for swimming pools. Some of the compounds of chlorine are equally valuable. In the Carrel-Dakin solution, one of the most important antiseptics, sodium hypochlorite, NaClO , is the active agent. Bleaching powder is another salt that is of interest as a disinfectant as well as a bleaching agent. Bleaching powder is made by the reaction of calcium oxide with chlorine as shown by the equation

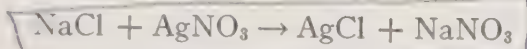


Compounds such as bleaching powder and Javelle water, NaClO , are used in manufacturing and in laundering cotton and linen goods. The use of these compounds as bleaching agents depends upon the liberation of hypochlorous acid as shown in the equation



The hypochlorous acid will give a clear white color to the fabric, but, unless washed out it has a deteriorating effect (Chapter XXXIV).

The Test for Chlorides, Bromides, and Iodides. — The chloride ion of hydrochloric acid or of chlorides may be identified in a solution by the reaction which is given with silver nitrate. The following equation shows the reaction:



The silver chloride formed in the reaction is a white curdy precipitate, insoluble in nitric acid. When a bromide or an iodide is used with silver nitrate, insoluble precipitates are formed which have a pale-yellow tint. The bromide and iodide ions may be recognized by the reaction previously given for the formation of bromine and iodine. If we consider the reaction of the salt with manganese dioxide and sulphuric acid, the color of the gas evolved is used as a means to identify bromine (brown gas) and iodine (purple gas).

QUESTIONS AND PROBLEMS

1. Give the formulas for the compounds in nature that are used as a source of each of the halogens. Describe briefly how the free element may be prepared from these compounds.
2. Describe the operation of the Nelson cell. What important substances are made from sodium chloride?
3. Compare the physical, chemical, and physiological properties of fluorine, chlorine, bromine, and iodine.
4. Write formulas and names of the four hydrogen halides as gases and as acids. Give the physical and chemical properties of the gases.
5. Write displacement reactions using chlorine with sodium bromide; chlorine with sodium iodide. Explain each reaction as oxidation-reduction.
6. Compare the reaction obtained when starch paste is treated with iodine and with iodide ion (in sodium iodide). Explain the difference in the reaction.
7. How may the sodium halides be distinguished by laboratory tests?
8. Write equations to illustrate the laboratory preparation of iodine, of hydrogen chloride, and of hydrogen fluoride.
9. Describe briefly the method of etching glass.
10. Write equations for the following reactions and tell what may be observed when each occurs:
 - (1) silver nitrate with potassium chloride
 - (2) concentrated sulphuric acid with sodium chloride
 - (3) concentrated sulphuric acid with sodium iodide (two steps)

- (4) silver nitrate with sodium iodide.
- (5) ammonia gas with hydrogen iodide
- (6) concentrated sulphuric acid with sodium bromide and manganese dioxide.
11. Write equations for the following reactions and describe the usefulness of the reaction:
 - (1) preparation of Javelle water from sodium carbonate and bleaching powder
 - (2) reaction of bleaching powder with carbonic acid.
12. Give one commercial use of a compound of each halogen.
13. How many grams of iodine can be obtained by the reaction of sulphuric acid and manganese dioxide with 50 grams of sodium iodide?
14. How many liters of hydrogen chloride gas will be formed from the action of sulphuric acid with 25 grams of calcium chloride?
15. Write the formulas for the following acids and the acid anhydride of each: hypobromous, bromous, chloric, and perchloric. Use graphical formulas to show the relationship of the acid to the hydroxide and to the acid anhydride.
16. Name the compounds: KBrO_3 , KClO_4 , NaClO , $\text{Ca}(\text{IO}_3)_2$, NaIO , $\text{Zn}(\text{ClO}_3)_2$, HIO_4 .
17. Write the formulas for:

calcium iodate	ammonium iodide
barium periodate	hypobromous acid
potassium hypochlorite	iodic acid
aluminium chloride	zinc bromate
sodium fluoride	bleaching powder
calcium chlorite	Carrel-Dakin solution.
18. Give the physiological importance of each of the halide ions.

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CHAPTER XXIII

THE PHOSPHORUS FAMILY

Introduction. — Reference to the periodic table tells us that the elements nitrogen, phosphorus, arsenic, antimony, and bismuth constitute a typical family in Group V. Nitrogen, an acid-forming element, is followed by phosphorus and arsenic, also acid-forming; amphoteric properties appear in antimony; bismuth is essentially base-forming. The study of this family of elements is interesting, not only because each element has individual characteristics and uses, but because it gives one a clear conception of the relationship between the position of an element in the periodic table and its properties. Since nitrogen has been studied quite fully in Chapter XIX, its properties will be discussed only in relationship to the other members of the family.

Occurrence of Each Element of the Group. — All bone matter contains phosphorus in the form of calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$. The salt occurs in great deposits of phosphate rock in Florida and other Southern States and also in Idaho and some of the surrounding States. It is probable that these deposits have their origin in the bones of animals and fish which at some time have collected there. Arsenic, antimony, and bismuth are widely distributed as sulphides. They are found in such compounds as arsenious sulphide, As_2S_3 , and antimonious sulphide, Sb_2S_3 , as well as in a form mixed with the sulphides of copper, lead, and other metals.

Preparation of Each Element of the Group. — Phosphorus is obtained from calcium phosphate, previously mentioned as the most abundant phosphorus compound. The finely ground phosphate rock, $\text{Ca}_3(\text{PO}_4)_2$, is mixed with sand, SiO_2 , and coke. The mixture is heated in an electric furnace. The reaction between the phosphate rock and sand is as follows:

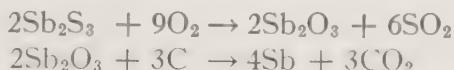


The phosphorus pentoxide is reduced by the carbon (coke) according to the reaction:



These two reactions go on together in the electric furnace. The calcium silicate is drawn off as a slag, and the phosphorus vapor is condensed to a liquid in cooling coils. The liquid phosphorus is collected in molds, where it becomes a crystalline solid.

Arsenic, antimony, and bismuth are obtained from their sulphides by the processes of roasting the ore to form the oxide, and then reducing the oxide with carbon. The following equations show a typical process, using antimony sulphide as an illustration:



Properties Characteristic of the Phosphorus Family. — Recalling the structure of the atoms of these elements, we know that each of these atoms has five electrons in the outer orbit. It follows that they may attract three electrons to complete the orbit of eight. This gives the elements a valence of negative three, as in the compounds NH_3 , PH_3 , AsH_3 , and SbH_3 . The elements may give up the five electrons and show a valence of positive five, as in the compounds N_2O_5 , P_2O_5 , As_2O_5 , and Sb_2O_5 . Apparently two of the electrons are held more tenaciously than the others, and the elements may give up but three electrons and show a valence of positive three, as in the compounds P_2O_3 , As_2O_3 , Sb_2O_3 , and Bi_2O_3 . Antimony and bismuth are increasingly metallic and usually show a valence of positive three.

A tabulation of the properties of the elements of the phosphorus family is shown in Table XX.

In addition to these properties, there are some which cannot easily be tabulated. The two allotropic forms of phosphorus are quite different. White phosphorus is crystalline and has a melting-point of $44^\circ \text{C}.$, below the boiling-point of water, and is soluble in carbon disulphide. It is chemically so reactive that it oxidizes in the air and spontaneously ignites. Therefore white phosphorus is always kept immersed in water. Red phosphorus is crystalline, it

TABLE XX

PROPERTIES OF THE ELEMENTS OF THE PHOSPHORUS FAMILY

<i>Property</i>	<i>Nitrogen</i>	<i>Phosphorus</i>	<i>Arsenic</i>	<i>Antimony</i>	<i>Bismuth</i>
Atomic weight	14.008	30.98	74.91	121.76	209
Atomic number	7	15	33	51	83
Color of solid	white solid (colorless gas)	white or red	gray	silvery	reddish
Allotropic forms		two or more	two	two	
Formulas	$\left\{ \begin{array}{l} \text{N}_2\text{O}_3 \\ \text{N}_2\text{O}_5 \end{array} \right.$ NH_3	$\left\{ \begin{array}{l} \text{P}_2\text{O}_3 \\ \text{P}_2\text{O}_5 \end{array} \right.$ PH_3	$\left\{ \begin{array}{l} \text{As}_2\text{O}_3 \\ \text{As}_2\text{O}_5 \end{array} \right.$ AsH_3	$\left\{ \begin{array}{l} \text{Sb}_2\text{O}_3 \\ \text{Sb}_2\text{O}_5 \end{array} \right.$ SbH_3	Bi_2O_3
oxides	$\left\{ \begin{array}{l} \text{HNO}_2 \\ \text{HNO}_3 \end{array} \right.$	$\left\{ \begin{array}{l} \text{H}_3\text{PO}_3 \\ \text{H}_3\text{PO}_4 \end{array} \right.$	$\left\{ \begin{array}{l} \text{H}_3\text{AsO}_3 \\ \text{H}_3\text{AsO}_4 \end{array} \right.$	$\left\{ \begin{array}{l} \text{Sb(OH)}_3 \\ \text{H}_3\text{SbO}_3 \\ \text{H}_3\text{SbO}_4 \end{array} \right.$	Bi(OH)_3
hydrides					
acids, bases	acid-forming	acid-forming	acid-forming	amphoteric	base-forming
or both					
Acid-forming, base-forming, or amphoteric					

has a high melting-point, it is insoluble in carbon disulphide, and it is not so reactive chemically. It is safely handled in the laboratory.

Arsenic is a brittle, crystalline metal. It is sometimes mixed with lead to make a hard alloy which is used in the manufacture of shot. Antimony is a metal which has the unusual property of expanding as it changes from liquid to solid form. When antimony is used in type-metal, this property of expansion gives a clear-cut face to the type. Bismuth has a very low melting-point and thus is useful as a constituent of the low-melting alloys used in fuse plugs and automatic water-sprinklers (Chapter XXVI).

The Hydrides of the Phosphorus Family. — With a valence of negative three, the elements form the following compounds: PH_3 , phosphine; AsH_3 , arsine; and SbH_3 , stibine. The hydride of bismuth is unstable. Of these hydrides, arsine is important as the basis of the Marsh test for arsenic compounds, described in a later paragraph.

The Acids of Each Element of the Group. — The reaction of an acid anhydride with water is one of the methods suggested in Chapter X for the preparation of acids. Phosphoric acid is thus formed according to the equation



The acid H_3PO_4 is often called **orthophosphoric acid** to distinguish it from two other phosphoric acids of which phosphorus pentoxide is the acid anhydride. When water is first added to phosphorus pentoxide, only one molecule combines, according to the equation



The acid formed is called **metaphosphoric acid**. If this solution is allowed to stand for several hours, two more molecules of water combine and orthophosphoric acid is formed. When orthophosphoric acid is heated, water is given up and another acid is formed, as shown by the equation



This acid is called **pyrophosphoric**. To correspond with these three phosphoric acids in which phosphorus has a valence of five,

there are three phosphorous acids in which phosphorus has a valence of three. The formulas and names of the acids of phosphorus are as follows:

P_2O_5 acid anhydride

H_3PO_4 orthophosphoric acid

HPO_3 metaphosphoric acid

$H_4P_2O_7$ pyrophosphoric acid

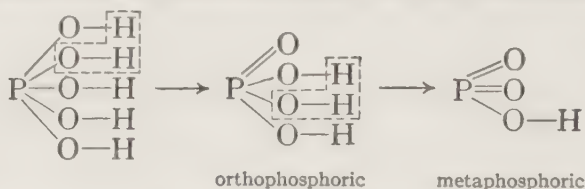
P_2O_3 acid anhydride

H_3PO_3 orthophosphorous acid

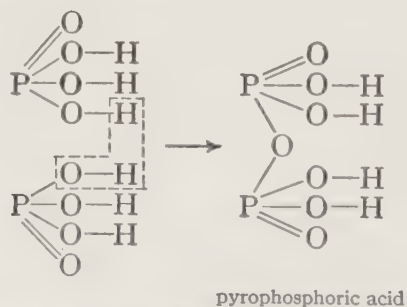
HPO_2 metaphosphorous acid

$H_4P_2O_5$ pyrophosphorous acid

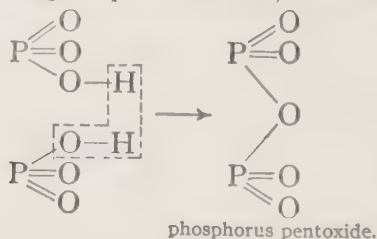
Most of the non-metallic elements in Groups III, IV, and V of the periodic table have a tendency to form several acids. In naming these acids, the prefix **ortho-** is given to the acid that contains the most water in combination, while the prefix **meta-** is given to the acid that contains the least water in combination with the acid anhydride. The formulas for the acids may be derived by withdrawing water from the hypothetical compounds $P(OH)_5$ or $P(OH)_3$ (Chapter XXI) as illustrated by the following:



Taking water from two molecules of the ortho acid gives pyrophosphoric acid:



The acid anhydride is obtained by withdrawing all the hydrogen as water from any of the phosphoric acids, for example:



If the symbols for arsenic and for antimony are substituted for phosphorus in the formulas just written, the series of acids formed by arsenic and antimony are obtained. The formulas and names of these acids are as follows:

As_2O_5 acid anhydride

H_3AsO_4 orthoarsenic

HAsO_3 metarsenic

$\text{H}_4\text{As}_2\text{O}_7$ pyroarsenic

As_2O_3 acid anhydride

H_3AsO_3 orthoarsenious

HAsO_2 metarsenious

$\text{H}_4\text{As}_2\text{O}_5$ pyroarsenious

Sb_2O_5 acid anhydride

H_3SbO_4 orthoantimonic

HSbO_3 metantimonic

$\text{H}_4\text{Sb}_2\text{O}_7$ pyroantimonic

Sb_2O_3 acid anhydride

H_3SbO_3 orthoantimonious

HSbO_2 metantimonious

$\text{H}_4\text{Sb}_2\text{O}_5$ pyroantimonious

Salts of These Acids. — The normal salts containing phosphorus, arsenic, and antimony are named from the corresponding acids. That is, the formulas and names of the normal sodium salts of the acids of phosphorus are as follows:

Na_3PO_4 sodium orthophosphate

NaPO_3 sodium metaphosphate

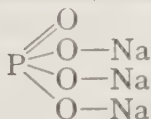
$\text{Na}_4\text{P}_2\text{O}_7$ sodium pyrophosphate

Na_3PO_3 sodium orthophosphite

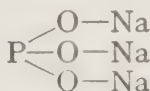
NaPO_2 sodium metaphosphite

$\text{Na}_4\text{P}_2\text{O}_5$ sodium pyrophosphite

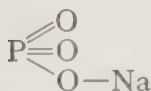
As graphic formulas, these salts may be written:



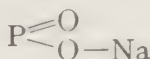
(sodium orthophosphate)



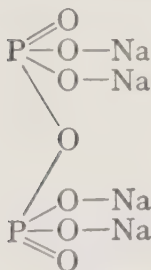
(sodium orthophosphite)



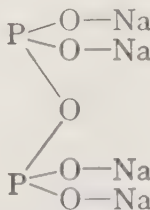
(sodium metaphosphate)



(sodium metaphosphite)

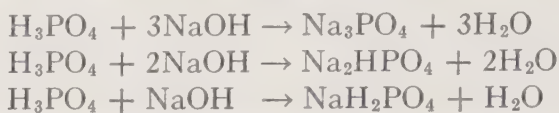


(sodium pyrophosphate)



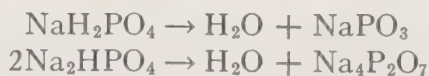
(sodium pyrophosphite)

Since orthophosphoric acid has three hydrogen atoms in its molecule, it may form two acid salts in addition to the normal salt, as shown in the following equations:



In order to distinguish between the two acid salts, the salt with the formula NaH_2PO_4 is known as sodium dihydrogen phosphate, monosodium phosphate, or primary sodium phosphate; and Na_2HPO_4 is called disodium hydrogen phosphate, disodium phosphate, or secondary sodium phosphate.¹ As indicated in the foregoing, the prefix *ortho*- may be omitted when naming the acid H_3PO_4 and its salts. The two calcium acid phosphates have the formulas $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and CaHPO_4 and are called primary calcium phosphate and secondary calcium phosphate respectively.

When acid salts are heated, there is always a tendency for them to decompose and give up water vapor. When the sodium acid phosphates are heated, salts of other phosphoric acids are formed by the removal of water, as shown in the following equations:



Phosphorus in the Home. — More than a century has passed since the days when a housewife started the fire with a spark made from flint and steel or obtained coals from the neighbors' hearth. To-day we enjoy the convenience of safety or of friction matches. The use of red phosphorus and of phosphorus sulphide (P_4S_3)

¹ The terms *primary* ("first in order") and *secondary* ("second in order") as used in these formulas need explanation. The first ionization of phosphoric acid is:



The sodium salt formed with this primary phosphate radical is NaH_2PO_4 , and is called primary sodium phosphate. When phosphoric acid ionizes according to the equation

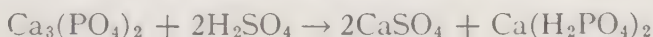


there are two hydrogen atoms replaceable by a metal. The sodium salt formed with this secondary phosphate radical is Na_2HPO_4 , and is called secondary sodium phosphate.

has played an important rôle in the development of a satisfactory mixture for use in the manufacture of matches. At one time yellow phosphorus was used. It caused a bone disease among the workmen, and various means of legislation were used to prevent the manufacture of yellow phosphorus matches.

The student of dietetics will immediately learn that food must contain phosphorus in order to supply calcium phosphate for bone tissue and phosphorus compounds for other cells. Nuts, whole wheat, eggs, milk, and legumes are rich in phosphorus.

Plants also need phosphorus compounds for proper growth and development, and for this reason much of the phosphate rock that is mined is used as fertilizer. Since plant roots cannot absorb the insoluble normal calcium phosphate rock found in nature, it is often converted to the more soluble primary calcium phosphate (superphosphate) by a reaction with sulphuric acid:



Calcium phosphate may be made available for plants also by conversion into ammonium phosphate. This compound is especially valuable as a fertilizer since it makes both nitrogen and phosphorus available in the soil.

Primary calcium phosphate is a component of certain types of baking-powders (Chapter XXXII); the compound is also used in common salt to prevent it from forming lumps in wet weather.

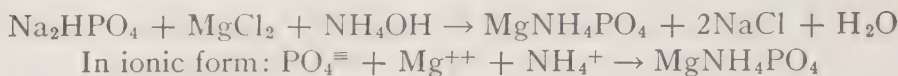
Normal sodium phosphate, Na_3PO_4 , has a strong alkaline reaction due to hydrolysis:



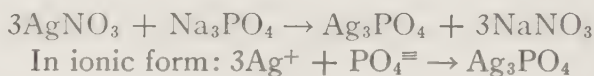
For this reason, sodium phosphate is a component of many types of washing powders used in cleaning utensils (Chapter XXXIII); sodium metaphosphate, in the complex form $(\text{NaPO}_3)_6$, is also a valuable component of certain cleaning mixtures.

Test for Phosphates. — The foregoing discussion of the importance of phosphorus in the body and hence in our foods emphasizes the need of practical tests for the phosphate radical. The following tests are characteristic:

1. With a magnesium salt in an alkaline (NH_4OH) solution, any orthophosphate ion gives a white, crystalline, or sandy precipitate of magnesium ammonium phosphate MgNH_4PO_4 . The equation for the reaction follows:



2. With silver nitrate solution, any orthophosphate salt gives a yellow precipitate which is soluble in acids. The precipitate is silver phosphate Ag_3PO_4 . The equation follows:



3. With ammonium molybdate, any orthophosphate ion gives a precipitate of characteristic formation. It is a brilliant yellow precipitate forming slowly as the mixture is warmed.

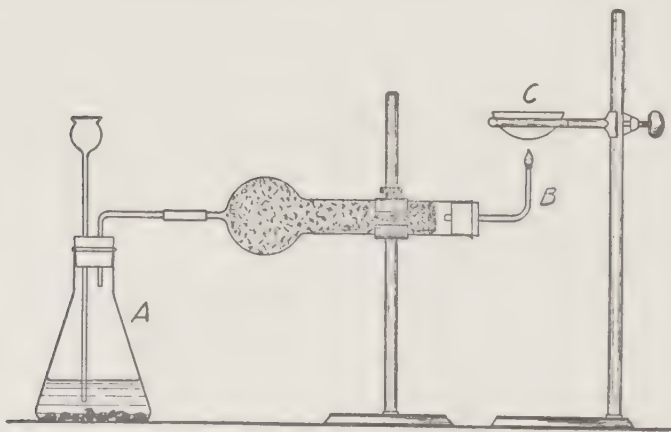
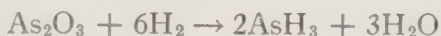


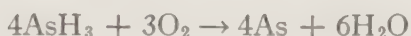
FIG. 36. Test for Arsenic

Test for Arsenic Compounds. — The poisonous property of arsenic compounds makes it necessary at times to detect their presence in food products. Small amounts of insecticides, such as Paris Green (copper acetoarsenite, $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Cu}_3(\text{AsO}_3)_2$),

which have been used as a spray to destroy moth and larvæ, may be present on cabbage, cauliflower, lettuce, celery, and the skins of many fruits. Rigid care should be used in the preparation of fruits and vegetables because the continued ingestion of small amounts of copper or of arsenic compounds cause the symptoms of poisoning — dry throat, skin eruptions, nausea and digestive disturbances. By a method, known as the Marsh test (Fig. 36) traces of arsenic compounds may be identified. A hydrogen generator A, using zinc (arsenic-free) and sulphuric acid, is prepared. A sample of the material containing arsenic is placed in the generator. The hydrogen formed by the reaction of the zinc and sulphuric acid reacts with the arsenic to form arsine, as shown by the following equation:

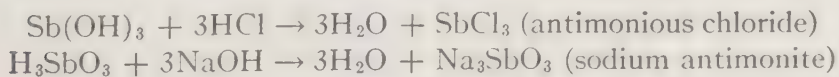


The gaseous product, a mixture of arsine and hydrogen, is burned at the glass tip B. The equation for the incomplete oxidation of arsine is:



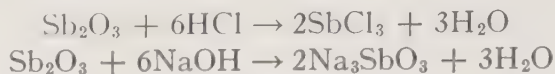
If a cold porcelain dish C is held in the flame of the burning gases, a black, metallic deposit of arsenic is formed. In a modified method, known as the Gutzeit test, the arsine is allowed to come in contact with mercuric bromide, with which it gives an orange color.

Amphoteric Hydroxides. — In our discussion of the periodic table it was shown that the hydroxides of many elements of Groups III, IV, and V have acid-forming and base-forming properties. They are called amphoteric hydroxides. Antimonious hydroxide shows this property and hence reacts with acids and with bases as shown by the equations:



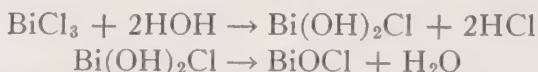
The same salts form when oxides react with acids and with

bases. Thus antimonious oxide dissolves in an acid and in a base according to the reactions:



Hydrolysis. — A review of the principles of hydrolysis will help in understanding the properties of salts of the phosphorus family. We have learned (Chapter XIV) that in hydrolysis a double decomposition reaction may occur between the ions of a salt and the hydrogen and hydroxyl ions of water. In a reaction of this type an acid and a base are formed. If the acid or the base, or both, are weak, hydrolysis occurs.

The elements of the phosphorus family form weak acids and bases, and as a result their salts undergo hydrolysis. The salts of bismuth and antimony hydrolyze in a slightly different way to other salts because of the formation of the insoluble basic salts, BiOCl or SbOCl , as precipitates. A typical reaction is:



or in one equation: $\text{BiCl}_3 + \text{H}_2\text{O} \rightarrow \text{BiOCl} + 2\text{HCl}$

These basic salts of bismuth and antimony form as heavy white precipitates when a solution (acidic) of the normal salt is poured into water. The reaction may serve as a means of detecting bismuth and antimony ions in solution.

QUESTIONS AND PROBLEMS

1. Give the formula for a compound in nature, containing each element of the phosphorus family. Write equations to show how the element is obtained from each of the compounds.
2. Write formulas and names for the hydrides of nitrogen, phosphorus, arsenic, and antimony.
3. Compare the properties of the two allotropic forms of phosphorus.
4. Using the valence of the element indicated by the periodic table, write graphic formula for the hydroxide of arsenic. Withdraw water from the hydroxide to show its relationship to the ortho and meta acid.
5. Use graphic formulas to show the relationship between orthoarsenic and pyroarsenic acids.

6. Write the following formulas, using the periodic table to determine valence. (In Groups III and IV, the formula for the ortho-acid is the same as the hydroxide; the formula for the meta-acid is obtained by withdrawal of one molecule of water from the ortho-acid.)

gallium hydroxide
stannic hydroxide
orthostannic acid
metastannic acid
aluminium hydroxide
metaluminic acid
sodium metaluminate

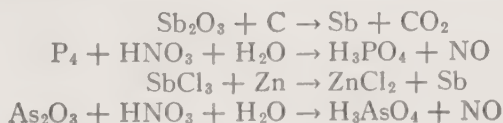
columbic hydroxide
orthocolumbic acid
metacolumbic acid
orthoboric acid
metaboric acid
orthosilicic acid
metasilicic acid

7. Write equations to show the preparation of arsine in the Marsh test, and for the burning of arsine in a limited supply of oxygen. What is observed in the Marsh test?
8. Write three equations to form the two acid salts and the normal salt by the reaction of orthophosphoric acid with sodium hydroxide. Name the salts.
9. Write equations to show the reactions of antimonious hydroxide with an acid; of antimonious hydroxide with a base. Name the salts formed. Write equations to show the reaction of antimonious oxide with an acid; of antimonious oxide with a base. Name the salts formed.
10. Name the following compounds: Na_3SbO_3 ; $\text{Na}_4\text{P}_2\text{O}_7$; NH_4PO_3 ; K_3PO_4 ; Na_2HPO_4 ; KH_2SbO_4 ; $\text{Mg}_2\text{P}_2\text{O}_7$; AsH_3 .
11. Write formulas for the following compounds:

disodium pyroantimonite
calcium orthoarsenate
monopotassium orthophosphate
zinc metaphosphate
potassium metarsenite

primary calcium phosphate
magnesium ammonium phosphate
barium pyroarsenate
antimonic sulphide
antimonious sulphide

12. Balance the following equations; what element is oxidized and what element is reduced?



13. Write equations for the following reactions:

- (1) disodium phosphate, heated
- (2) monosodium phosphate, heated
- (3) sodium pyrophosphate with silver nitrate
- (4) sodium orthophosphate with silver nitrate.

14. Write equations to show the hydrolysis of antimonious chloride; of bismuth chloride. What is observed when the reactions occur?
15. Describe two tests for phosphate ion. Write an equation for the reaction of the test with magnesia mixture.
16. How many grams of primary calcium phosphate will be formed by the reaction of 240 c.c. of tenth-normal phosphoric acid with calcium hydroxide?
17. At 25° C. and 720 mm. pressure, 286 c.c. of arsine gas weigh 0.87 gram. Use the data to determine the gram-molecular weight of arsine.
18. How many c.c. of fourth-molar secondary sodium phosphate will react with magnesium chloride and ammonium hydroxide to form a precipitate of 0.4520 gram of magnesium ammonium phosphate?
19. What is the percentage of phosphorus in primary and in secondary calcium phosphate?
20. Write equations to illustrate the following preparations:
 - (1) dipotassium antimonate from orthoantimonic acid
 - (2) trisodium pyrophosphate from pyrophosphoric acid
 - (3) monosodium antimonite from antimonious acid
 - (4) disilver orthoarsenite from orthoarsenious acid
 - (5) metarsenious acid from its acid anhydride
 - (6) pyroantimonic acid from its acid anhydride
 - (7) orthovanadic acid from its acid anhydride
 - (8) orthogermanic acid from its acid anhydride
 - (9) sodium metaphosphate from monosodium orthophosphate
 - (10) antimonious sulfide from antimonious chloride
 - (11) orthoboric acid from its acid anhydride
 - (12) metaphosphoric acid from its acid anhydride
 - (13) nitric acid from its acid anhydride

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CHAPTER XXIV

METALLURGY

SHALL we choose a new ring made of silver, gold, or platinum? Shall the new tea-kettle be made of cast aluminium, copper, tin, or stainless steel? What metal will we have in the new stove, sewing machine, tea-service, or tableware? In estimating the usefulness of a metal in the home, it is the physical properties — density, malleability, hardness, metallic luster, and ability to conduct heat and electricity — that must be considered. The only chemical property that is especially desirable in a metal used in the home is a lack of chemical activity or resistance to corrosion.

In chemistry these physical properties are of secondary interest only, and the chemical reactions are the most important. The chemical properties of typical metals may be summarized as follows:

1. Metals give up electrons easily, thus forming the positive ion of a base or salt.
2. The metals and the oxides of metals that are soluble in water react with it to form bases. The most active metals form the strongest or most highly ionized bases.
3. Metals above hydrogen in the electrochemical series (the more active metals) displace hydrogen from acids in dilute solution to form salts.
4. Oxides and hydroxides of metals react with acids to form salts.
5. In electrolysis, the metallic ions migrate to the cathode or negative electrode.

Many of the metals most familiar to us, as copper, aluminium, and zinc, are not classed in chemistry with the more typical metals, since they give up their electrons with some difficulty and form only slightly ionized bases. On the other hand, the elements

that have the chemical properties of typical metals, such as sodium, cannot be used in the home or industry because they are active chemically and react with water vigorously. In other words, the metals that are least useful in the form of elements are, as a rule, most interesting in chemistry because of their high reactivity and ability to form diverse compounds.

In the following chapters, we shall find that the metals of the Sodium Family of Group I in the periodic table have the most typical chemical properties of metals. The element cæsium, the heaviest metal of the Sodium Family, gives up electrons most readily and is the first metal in the electrochemical series. It is followed in activity by the other elements of the family. Surprising as it may seem, the elements of the Copper Family in the same group are among those with the least typical chemical properties and thus are most useful as metals. They are found at the end of the electrochemical series.

Metals have become so much a part of our daily lives that we seldom realize how much the chemical and industrial laboratories have done for us in making them available to-day. Compare our lives with that of the cave-man who used only stone implements for household utensils, or with that of our grandmother using heavy, cumbersome iron kettles with possibly a few brass utensils, not so safe to use because poisonous copper salts are formed when food is left in them too long. Only the wealthy could afford to have shiny silver dishes. To-day we find in every home a variety of metals — chromium-plated trays and dishes, aluminium kettles, silver-plated tableware, stainless steel knives, monel metal faucets and table tops, and brass lamps. Even those who are not wealthy have gold and platinum jewelry. Many less familiar metals are of importance to us too, as the tungsten filament in our electric light bulb, the iridium tip on our fountain pen, and the mercury in our thermometer.

All these metals come from minerals that look very different from the metal. The metals that are non-corrosive and inactive, such as those of the Copper Family and the Platinum Group, are found in mines uncombined with other elements. They are said to occur "free" or "in the native state." Although they occur as

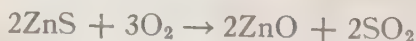
metals, the average person might pass them by without seeing them because of the great excess of rock or sand with which they are mixed. Most of the other metals occur as oxides or sulphides, often mixed with rock. Iron mines are usually deposits of red-brown iron oxide. Lead and zinc sulphides, black and reddish crystals, are often found together, mixed with quartz. Aluminium, the third most abundant element and the most abundant metal in the earth's surface, occurs everywhere as complex silicates known as clay. In a few places it occurs as an impure aluminium oxide in the form of a brown powder. It is from this brown powder that the metal aluminium is obtained to be used in kettles, sewing machines, and streamlined trains.

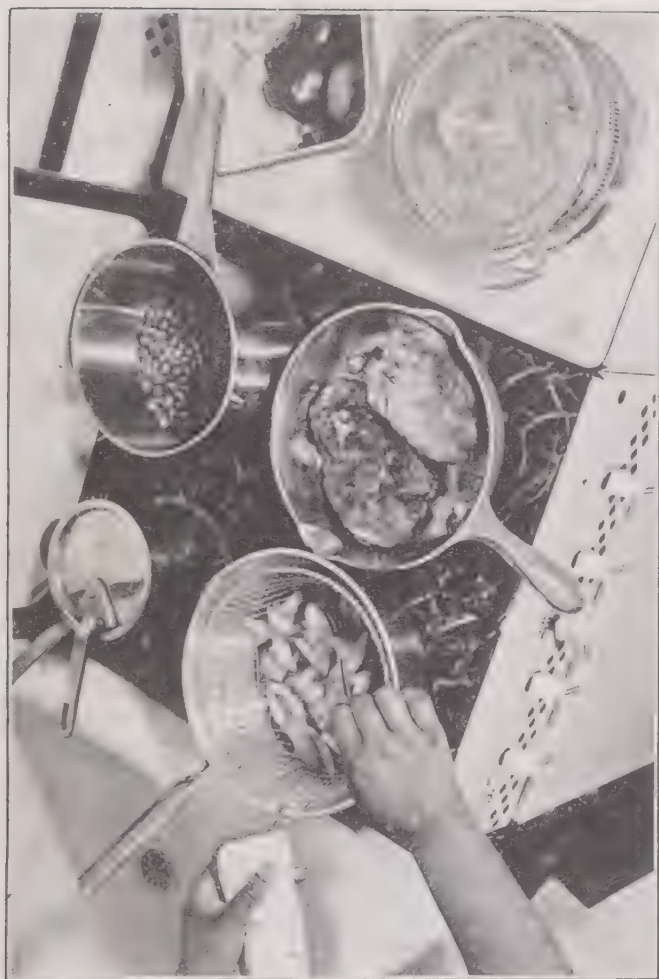
The very active elements of the Sodium Family occur in nature as a variety of compounds, while those of the Calcium Family occur as carbonates and sulphates. Just as these two families of metals combine most easily with other elements, these metals also are the most difficult to separate from their compounds. However, because of their activity, they are less often wanted as metals.

Metallurgy, or the reduction of the metallic ore to the pure metal, is an important application of chemistry to industry. The following outline of the general methods in use will indicate the chemical reactions involved and the necessity of chemical control in adapting the general methods to the different kinds of ore used.

1. *Concentration*. This involves the process by which the metal or its compound is separated from the rock, gravel, clay, sand, or other material with which it may be associated in nature. Gold can be separated from the lighter sand, with which it is often mixed, by repeated washings with water. This is called "panning gold." In some cases the ore is carried along a belt and the crystals of oxide or sulphide are picked from it by hand.

2. *Roasting the Ore*. (Chapter XXV, Table XXI.) The process of heating certain ores in air changes them to oxides. Sulphide ores are treated in this way, the following change taking place:



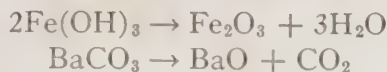


From *Life Magazine*, courtesy of Pictures, Inc.

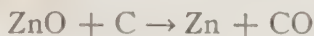
METALS IN THE KITCHEN

The picture shows kitchen utensils made of a variety of metals. Potatoes fry in an aluminum deep-fryer; veal cutlets are browned in a cast iron skillet; peas cook in a stainless steel pot; sauce simmers in a copper pan. Aluminum's first great use was in the kitchen. It quickly pushed cast iron aside because it was lighter and easier to clean. Steel is now taking the place of iron in making a strong clean-surfaced stainless steel ware. Aluminum conducts heat better than steel (*Life Magazine*, June 5, 1939).

Carbonates and hydroxides when heated strongly also change to oxides. This is represented by the equations:

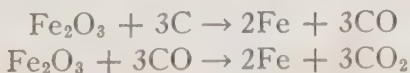


3. *Reduction of the Oxide.* (Chapter XXV, Table XXI.)
(a) *With carbon:* Iron oxide, zinc oxide, and many other oxides when ground and heated with carbon are reduced to the free metal. Usually carbon monoxide is formed in this reaction because of the limited supply of oxygen in the ore. A typical equation is:



This process is well illustrated by the metallurgy of iron. Deposits of red, yellow, and black iron oxide occur in layers underneath the soil in many countries. In the United States, one of the largest deposits being worked is in northern Minnesota and Michigan near Lake Superior. The iron ore (iron oxide) is removed from the mines by digging large open pits or by underground tunnels. It is carried on barges to the industrial centers where steel mills are located. Since coal is used in the reduction of iron ore, a desirable location for a steel mill would be where deposits of coal are available.

Blast furnaces (Fig. 37) eighty feet or more in height, built in the shape of a cylinder bulged near the bottom, are used. A mixture of coke, limestone, and iron ore is added through a trap-door opening in the top of the furnace; a blast of air is forced through the mixture by means of openings at the bottom. The coke starts burning at the bottom, and a variety of chemical reactions take place throughout the mixture. Some of the heated carbon forms carbon monoxide, because the lack of oxygen in the furnace prevents its complete oxidation. This carbon monoxide and some of the heated carbon reduce the heated iron oxide at the center of the furnace. Some of the equations are:



In the meantime the heated limestone combines with the sand and other impurities of the iron ore forming a liquid known as slag. This is lighter than the melted iron. As the drops of melted iron form from the reduction process, they settle through the slag

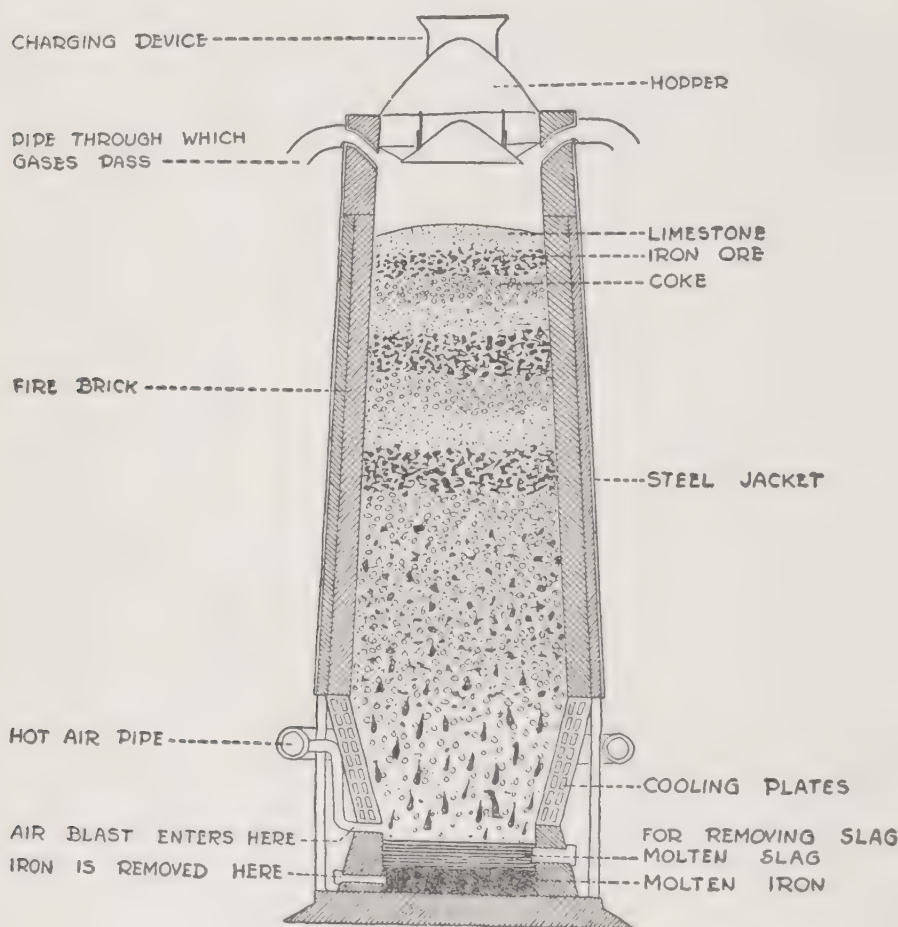


FIG. 37. Blast Furnace

to the base of the furnace. (A portion of it combines with carbon to form iron carbide, and some impurities are dissolved.) Occasionally the slag and the melted iron are drawn off from the bottom and more of the ore, coke, and limestone mixture is added

from the top. In this way the reduction continues without interruption until the furnace is worn out.

The iron drawn off from the blast furnace is either run into molds and sold in this form as "pig" or cast iron, or it is further treated to form wrought iron or one of the many forms of steel. All the operations are carried out on a large scale, and the great furnaces and crucibles of melted metal, carried by overhead pulleys or by small railroads and tipped or poured in ton lots, make a picturesque scene.

(b) *With aluminium*: Some oxides of metals are so stable that they resist reduction with carbon; others may combine with the carbon to form carbides. The German chemist, Goldschmidt, perfected a process in which aluminium is used as the reducing agent. Oxides of chromium and manganese are reduced in this way.



4. *Electrolysis*. (Chapter XXV, Table XXI.) The process of electrolysis is often used for the refining of metals where the pure element is needed. It is also necessary for the separation of the more active metals.

(a) *Electrolysis in water solution*: This method is applicable to the refining of copper, gold, silver, and other metals (Chapter XIII). The process for obtaining copper illustrates the method. Crude copper plates (called blister copper) are suspended in tanks in a water (with sulphuric acid) solution of copper sulphate. The blister copper is made the anode, and a thin sheet of pure copper is used as the cathode. The copper ions of the dissolved copper sulphate are attracted to the cathode where they gain electrons and become copper atoms which deposit on the pure copper cathode. The sulphate ions travel to the anode, where they dissolve copper from the blister copper plate. These changes are (1) at the cathode,



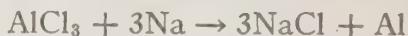
and (2) at the anode,



This change will continue until the blister copper plate is dissolved. Insoluble impurities from it will deposit on the bottom of the tank.

(b) *Electrolysis of a fused salt*: This method is applicable to the preparation of the active metals, such as cæsium, sodium, potassium, and calcium. They form compounds so stable that they may not be reduced readily by reducing agents. The commercial preparation of sodium illustrates the process of using electrolysis of fused salts; for example, melted sodium chloride (with the addition of traces of calcium chloride to lower the melting-point) is used as the source of sodium. The container holds strips of iron or copper as the cathode, and a graphite anode. Iron gauze between the cathode and anode serves to separate the products of the reaction as they are formed. As electrolysis occurs, the chlorine gas is collected at the anode and melted sodium is liberated at the cathode. The sodium collects in a reservoir in which the metal is protected from oxidation.

The most interesting application of electrolysis is the process used for the preparation of aluminium discovered by Charles Martin Hall in 1886. Previous to this time, the pure metal had been prepared only by displacement of aluminium from its salts by the more reactive, but expensive, metal sodium:



Samples of the metal were then kept in museum cases and could be obtained only at a cost of fifteen dollars a pound. Although aluminium is the most abundant metal in the earth's crust, in the form of clay and rocks, housewives had to use heavy black iron kettles and utensils until the chemist devised a convenient method for preparing the pure metal from its compounds.

While Charles Martin Hall was a student at Oberlin College, his professor stated during a lecture that the man who discovered how to prepare aluminium would benefit society and make a fortune for himself. Hall said to the student next to him, "I'm going after that metal." After graduation in 1885, he continued working on aluminium compounds in his mother's woodshed, using mostly home-made apparatus. On February 23, 1886, using



Courtesy of Anaconda Copper Mining Company

ELECTROLYTIC REFINING OF COPPER

The picture shows the tank room of the electrolytic refinery at the Anaconda copper plant at Great Falls, Montana. The view includes a section of copper cathodes as they are lifted from the tanks.

an electrolytic process, he obtained a few pellets of aluminium. Since the same process has been developed on a commercial scale, aluminium has been prepared so as to sell at eighteen cents a pound.

The electrolytic process devised by Hall consists in dissolving pure aluminium oxide in melted cryolite, Na_3AlF_6 and passing an electric current through the solution. The vessel containing the solution is used as the cathode, and carbon rods hanging in the bath serve as the anode. Aluminium, being positive, collects on the sides and bottom of the vessel and can be drawn off as liquid metal (Fig. 38).

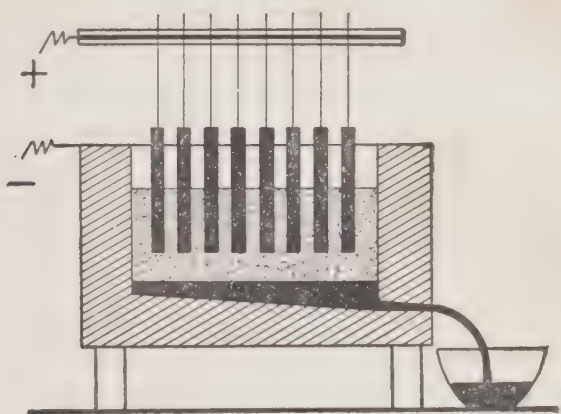


FIG. 38. Preparation of Aluminium

QUESTIONS AND PROBLEMS

1. What properties of sodium indicate that it should be classified as a metal? What chemical properties of aluminium indicate that it is not a typical metal? What chemical property makes gold a valuable metal?
2. List four metals that occur free. List two metals that occur abundantly in compounds of each of the following types: chlorides, carbonates, sulphides, oxides.
3. List the four steps in metallurgy. Write equations for the reactions that occur in roasting zinc ore; in reducing iron oxide; in reducing zinc oxide; in reducing chromium oxide.
4. Make diagrams to show the metallurgy of iron, of copper, and of aluminium. Briefly describe each process.

CHAPTER XXV

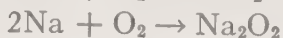
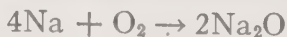
THE METALLIC ELEMENTS AND THEIR COMPOUNDS

ALTHOUGH all metals have certain properties in common, they differ from each other almost as much as the non-metallic elements. Each metal has individual properties that fit it for certain uses and make it individually important to our daily comfort. Moreover, each metal forms compounds with individual properties that make them valuable. In this chapter we shall make a survey of the metals and their important compounds, with especial reference to their uses. The United States is fortunate in having rich natural resources, making it independent of other countries for its supply of most minerals. However, it is still dependent on other countries for tin, nickel, chromium, antimony, platinum, and asbestos. A study of Table XXI will show where we obtain these.

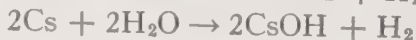
SODIUM FAMILY, GROUP I—LITHIUM, SODIUM, POTASSIUM, RUBIDIUM, CÆSIUM

Properties and Uses of the Metals. — Because of their great reactivity these metals are seldom seen as elements. A sample of any one of them must be immersed in kerosene to prevent it from reacting with the moisture in the air and igniting spontaneously.

Since atoms of all these metals have one electron in the outer orbit of the planetary system, they are monovalent in their compounds. Combination of the element with oxygen forms the oxide or the peroxide, as shown by the equations:



The metals react with water to form hydrogen gas and a strong base as shown by the equations:



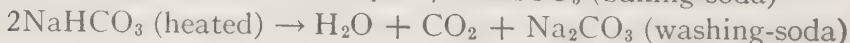
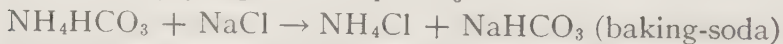
All of these metals form strong bases and are called the "alkali metals." Because of their reactivity these elements have few uses as metals. Lithium is used in some alloys. Sodium metal is in demand for the laboratory synthesis of complex organic compounds. Rubidium and caesium are used in photoelectric cells and vacuum tubes because of the ease with which they emit electrons. In the vacuum tubes they combine with the remnant of air that cannot be removed by mechanical means. In the photoelectric cell a film connected with an electric circuit is coated with the metal. Whenever light falls on this metal, electrons are emitted, causing an electric current in the circuit. The sound that accompanies motion pictures depends on the electric current developed by such a photoelectric cell which receives light through a wavy line printed at one side of the picture film.

Important Compounds. — The compounds of sodium and potassium are very important. Many of them, as well as compounds of calcium and magnesium, occur in large deposits where in the past salt lakes or oceans have evaporated (Table XXI). As the water evaporated, certain ions became concentrated enough to precipitate a slightly soluble salt, and a layer of the salt would deposit in the bed of the lake. Later, with more evaporation the water again became saturated with different salts which precipitated in other layers. One of the most noted deposits of this type is at Stassfurt, Germany, from which many countries obtained their supplies of potassium and magnesium salts. Lake Magadi in British East Africa has large deposits of sodium carbonate, and in Saskatchewan, Canada, is a large deposit of sodium sulphate. In this country, California has several deposits that furnish sodium carbonate, borax, calcium sulphate, and potassium chloride, all of which are important compounds. Another large deposit of salts is found where a large salt lake evaporated near Carlsbad, New Mexico. The calcium carbonate was first deposited because it was the most insoluble salt. As water washed through the calcium carbonate, it was dissolved away from the other layers of rock and thus formed a huge cave, the mammoth Carlsbad Caverns. Near these caves are quantities of common salt and an

abundant deposit of potassium chloride. Before the discovery of this deposit of "potash" the United States was dependent on the Stassfurt deposits in Germany for this compound, or on less rich sources in certain California lakes and in the ashes of certain plants. Smaller deposits of salts are found in Wyoming and North Dakota.

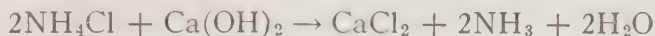
Probably sodium chloride, or common salt, is the most important compound of sodium, not only because of its abundance but because it is a necessity in our daily nutrition. Moreover, it makes foods more palatable and acts as a preservative. In industry it is used as a basis for preparing other important sodium compounds that do not occur in sufficient abundance in nature. It is fortunate that sodium chloride is widely distributed throughout the world, either in underground mines or in salt lakes or oceans.

Sodium carbonate, Na_2CO_3 (washing-soda), is an important constituent of glass and soap. It is used in the manufacture of paper, textiles, petroleum, and sodium salts. In the home and in many industries it is an important water softener. Because the naturally occurring deposits are not sufficient for the demand, much of the sodium carbonate is manufactured from sodium chloride by a method called **the Solvay process** after its originator. This method depends upon the reaction of salt with carbon dioxide and ammonia. Sodium bicarbonate, which is the least soluble salt in the reaction, is formed as a precipitate. When sodium carbonate is desired, the sodium bicarbonate is decomposed by heat into the normal carbonate. The reactions are as follows:



The materials used for the production of sodium carbonate by the Solvay process are not expensive. Sodium chloride is the source of the sodium ion. Carbon dioxide is obtained by heating calcium carbonate, or by burning coke. The ammonium chloride which is a product of one of the reactions is treated with slaked lime to

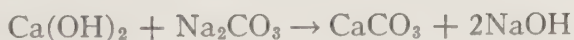
form the ammonia gas used in the first step of the process. The equation for this reaction follows:



Sodium bicarbonate, NaHCO_3 , or baking-soda, is also prepared by this process. This salt is used as a mild base and as a leavening agent in the home. Its chief use in industry is in the preparation of baking-powders and drugs that effervesce when added to water.

Sodium sulphate, Na_2SO_4 , is used as a substitute for sodium carbonate in the manufacture of glass and is important in the preparation of certain wood pulps for paper; when it is used as a drug, called Glauber's salt, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, it acts as a laxative. Many mineral waters owe their laxative action to the presence of this salt.

Borax, or sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, is used in laundries and as a basis for the preparation of boric acid, H_3BO_3 . Sodium nitrate, NaNO_3 , called Chile saltpeter because it comes from deposits in Chile, is an important fertilizer. Sodium hydroxide, lye or caustic soda, is an important base in industry and in the home. It is made by the Nelson cell (Chapter XXII) or by the action of slaked lime with washing-soda. The equation for this process is:

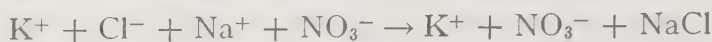


The formation of a precipitate CaCO_3 , causes the reaction to go to completion.

Sodium silicate, or water glass, Na_2SiO_3 , is a viscous liquid in solution that is used as an egg-preserving liquid, as a glue, and as a water softener. Sodium orthophosphate, Na_3PO_4 , and sodium metaphosphate, NaPO_3 , are used in washing-powders because they hydrolyze to give a basic reaction and because they are water softeners. Sodium hypochlorite, NaClO , or Javelle water (Chapter XXII), has been studied as a bleaching agent. All these compounds can be prepared from the action of sodium carbonate with the corresponding calcium salts.

Potassium nitrate, KNO_3 , is now prepared from the potassium

chloride obtained from New Mexico. When this salt is heated with sodium nitrate and the hot solutions are concentrated, the sodium chloride is the least soluble salt and precipitates:



If sodium chloride is filtered off, the potassium nitrate may be crystallized easily from the cooling filtrate. This process is possible because the sodium chloride does not increase in solubility in hot solutions, while the potassium nitrate does. The potassium nitrate, called saltpeter, is a constituent of black gunpowder and is a good fertilizer.

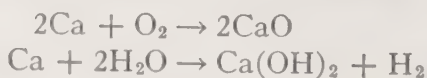
Much of the potassium in the earth's crust is in the form of feldspar, potassium aluminium silicate, KAlSi_3O_8 , which hydrolyzes to form a clay that furnishes some of the potassium ions needed for plant life.

The compounds of lithium, rubidium, and caesium are comparatively rare and of little importance commercially. Lithium salts occur in certain mineral waters and were once supposed to have medicinal properties. Lithium chloride is deliquescent and is used in air conditioning to reduce relative humidity (Chapter XVIII).

THE CALCIUM FAMILY, GROUP II — CALCIUM, STRONTIUM, BARIUM, RADIUM

Properties and Uses of the Metals. — Calcium, strontium, and barium are known as the alkaline earth metals. Radium has many of the properties of the other elements but, because of its radioactive properties, it and similar elements following it in the periodic table will be studied in Chapter XXVIII.

The alkaline earth metals are similar in all their properties to the alkali metals but are divalent in their compounds and exhibit their properties with less intensity. They oxidize readily to form the oxide and react with water to form hydrogen gas and a base. The following equations illustrate the reactions:



The metals, like sodium, are kept under oil and have few industrial uses except in unusual alloys and as a "getter" to remove the oxygen from vacuum tubes. Calcium, the least expensive and most abundant of these metals, is used like aluminium as a reducing agent in the metallurgy of certain active metals such as beryllium.

Important Compounds. — Calcium carbonate, CaCO_3 , the most abundant compound of calcium, occurs in many forms — in sea-shells, coral, pearls, marble, and chalk. It is most abundant as layers of limestone or as rock-like formations in caves found in the beds of evaporated oceans.

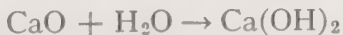
Other naturally occurring compounds of calcium are calcium sulphate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, called gypsum, used as a building stone and in making plaster of Paris, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$; calcium magnesium silicate, $\text{CaSiO}_3 \cdot 3\text{MgSiO}_3$ or asbestos; calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, used in fertilizer (Chapter XXIII); and calcium fluoride, CaF_2 , which is a source of fluorine and also is of use in metallurgy, since it helps melt certain ores.

Calcium carbonate is used in preparing other calcium salts, in the manufacture of sodium carbonate by the Solvay process, and in making glass. In the form of a powder (precipitated chalk), it is used as a polishing material, as an inexpensive white pigment in paints, and as a constituent of tooth powders and toothpastes.

Calcium oxide is made by heating limestone, CaCO_3 , as shown by the equation:



Calcium oxide (quicklime) is important in the manufacture of bleaching powder, cement, calcium carbide, and insecticides. It reacts with water to form calcium hydroxide:



Calcium hydroxide is a slightly soluble, inexpensive base which has many industrial uses, such as in making plaster, in manufacturing sodium hydroxide and other bases, and neutralizing acidity in soils. Solid calcium hydroxide is slaked lime; as a saturated solution, it is known as lime-water.

Strontium and barium compounds are less abundant than those of calcium and for this reason have fewer commercial uses. Their salts, as well as those of the alkali metals, burn with colored flames and are valuable in coloring fireworks. Strontium hydroxide, $\text{Sr}(\text{OH})_2$, is used in refining sugar. When added to sugar solutions, a compound is formed which crystallizes and may be separated from the solvent. To recover the sugar, the strontium-sugar compound is suspended in water and the strontium is precipitated as the carbonate by the addition of carbon dioxide. This precipitate is then filtered off, and the sugar solution is obtained by evaporating the filtrate.

Barium hydroxide, $\text{Ba}(\text{OH})_2$, is preferable to lime-water for some laboratory reactions, because it is more soluble and hence more effective as a base. Barium sulphate, BaSO_4 , is the most abundant mineral source of barium. Since it is insoluble, it can be used as a pigment in white paint and as a filler in oilcloth, linoleum, and paper.

MAGNESIUM FAMILY, GROUP II — BERYLLIUM,
MAGNESIUM, ZINC, CADMIUM, MERCURY

Properties and Uses of the Metals. — The metals in this family are alike only in their valence and the properties of some of their compounds. Beryllium resembles aluminium in Group III; magnesium resembles calcium, while mercury is a noble metal like copper, silver, and gold.

Beryllium is a light gray, hard metal, lighter than aluminium, with a very high melting-point. When mixed with other metals as alloys, it gives them desirable properties. It is especially valuable in the preparation of light, strong metals for aircraft, and in metals used to conduct electricity. Because it occurs only in complex silicates, it has been difficult to prepare as an element. At present, methods are being developed to prepare it by electrolysis in quantities large enough to be of use commercially.

Magnesium is a light-weight silvery metal, which forms strong, non-corrosive alloys (Chapter XXVI). In the form of a powder or ribbon, it burns with a white flash of light. For this reason, magnesium finds use in flashlight photography. It does not react

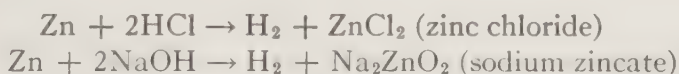
with cold water but reacts with steam or boiling water according to the equation:



Zinc is less reactive than magnesium and is valuable as a metal. Although zinc oxidizes easily on the surface, the oxide forms an adhesive coating which protects the metal from further corrosion. Iron is often coated with a thin layer of zinc (galvanized iron) to prevent the formation of iron rust. Containers made of galvanized iron are not suitable for exposure to steam, however, since the zinc, like magnesium, reacts slowly with steam to form the oxide:

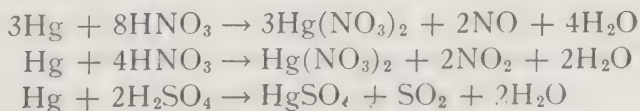


Zinc reacts also with dilute acids and with bases according to the reactions:



Cadmium, like zinc, is not a reactive element and gives desirable properties to many alloys (Chapter XXVI). Cadmium plated on iron makes a product that is more rust-resistant than galvanized iron.

Mercury has less reactivity than many other metals, and to some extent occurs free and in the form of gold and silver amalgams. Cinnabar, or mercuric sulphide, is the most important mercury ore (Table XXI). Mercury is unique in that it is a liquid metal, a fact which makes possible its use in thermometers and barometers. It is chemically inactive towards oxygen, water, and dilute acids. Concentrated oxidizing acids react with mercury by reactions characteristic of these acids:



Important Compounds. — Beryllium is present in certain precious stones such as emeralds and beryls which are beryllium aluminium silicate, $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$.

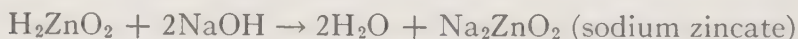
Magnesium and calcium compounds often occur together as in a native rock, $\text{CaCO}_3 \cdot \text{MgCO}_3$, which is an excellent building stone, and in asbestos, $\text{CaSiO}_3 \cdot 3\text{MgSiO}_3$, which is a heat insulator. Other familiar compounds of magnesium are milk of magnesia, or magnesium hydroxide, $\text{Mg}(\text{OH})_2$, and Epsom salts, or magnesium sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. Magnesium oxide, MgO , a white powder, has important uses as a lining for high temperature furnaces and heat insulators.

Zinc sulphide, ZnS , and zinc carbonate, ZnCO_3 , are the most abundant ores of zinc (Table XXI). From these, the compounds of zinc needed in industry are made. Zinc compounds are poisonous and so have important uses as disinfecting fluids. Zinc oxide, mixed with a soft oil, is an antiseptic and healing salve.

Zinc hydroxide is amphoteric. As a base it reacts with an acid:



As zincic acid, H_2ZnO_2 , it reacts with strong bases to form a soluble salt:



The white paint pigment, lithopone, is formed by the reaction of zinc sulphate and barium sulphide, according to the equation:



Both products, zinc sulphide and barium sulphate, are white and insoluble. Hence, when mixed with linseed oil in the preparation of white paint, they give a durable paint of good covering power. As a white pigment, zinc compounds are in competition with basic lead carbonate. Paints have to stand much weathering and exposure to gases, of which hydrogen sulphide is more or less prevalent. A lead paint darkens when exposed to hydrogen sulphide because of the formation of lead sulphide, PbS (black). On the other hand, a zinc paint containing zinc sulphide (white) or zinc oxide either remains the same in composition or changes from zinc oxide to zinc sulphide but does not change in color.

Cadmium and mercury also form paint pigments; cadmium sulphide, CdS , yellow, and mercuric sulphide, HgS , vermilion red.

Mercury forms two series of salts, mercurous, Hg^+ , and mercuric, Hg^{++} ; for example, calomel is mercurous chloride, HgCl , and bichloride of mercury is mercuric chloride, HgCl_2 . Many mercury salts are poisonous. All of them are volatile, and, if the vapors are inhaled, they poison the body. Soluble salts also are easily absorbed and very poisonous. Mercury salts find uses as disinfectants, antiseptics, and medicines. Thus if used under proper supervision, they are human benefactors. They may be used also for man's destruction — industrial workers often become poisoned by using mercury compounds in paints, in percussion caps, and in preparing hair for felts.

ALUMINIUM, GROUP III

Properties and Uses of the Metal. — It was the dawn of a new day for the housewife when aluminium utensils replaced the black unattractive iron pots and pans in the kitchen. Since aluminium came out of the museum cases and began to be used commercially, it has answered the requirements for many purposes — parts of automobiles, airplanes, wrapping foil, streamlined trains, electric wires, household utensils, and many alloys. The properties which make aluminium especially desirable are its lightness, silvery luster, malleability, and ductility. It is a good conductor of heat and electricity. Like zinc, aluminium does not corrode in the air because an oxide film forms and adheres to the surface as a protective coating. Aluminium reacts readily with dilute acids and with bases as shown by the equations:



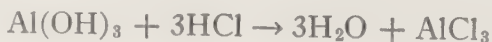
Reference to the effect of cooking fruits and vegetables in aluminium vessels was made in Chapter XIV. Fruit and vegetable acids, especially in the presence of sodium chloride, slowly dissolve the metal, forming soluble aluminium salts. It follows that when acid fruits or vegetables are cooked in an aluminium

vessel, they contain aluminium ions in solution. The concentration of these compounds is small, however, and experiments in feeding large amounts of soluble aluminium salts to animals and to man have shown no harmful effects. Scientists generally believe that their presence in food should cause no concern.

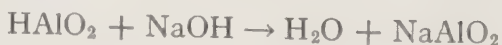
Housewives object to aluminium ware because of the formation of a dark surface when aluminium is in contact with hard water or alkaline solutions. The cause of this darkening is not definitely known, but an explanation may be offered. It is probable that the metal used for aluminium utensils contains some iron. The aluminium is dissolved by an alkaline solution, in which iron is insoluble. It follows that, when washing-soda stands in an aluminium vessel, some aluminium may be dissolved, leaving colloidal iron as a black deposit on the surface. Iron is soluble in acids, and when a fruit juice or vinegar is heated in the utensil, the iron coating will dissolve and again the aluminium utensil becomes bright. Special washing-powders are sold for cleaning aluminium ware. They contain water-glass, Na_2SiO_3 , as a protective colloid to inhibit the action of the alkaline washing-soda, Na_2CO_3 , on the metal.

Aluminium in the form of complex compounds such as feldspar, mica, and clay, makes up 7.3 per cent of the earth's surface. It is surpassed in abundance only by oxygen and silicon. Aluminium metal and the compounds that are needed commercially are made from an impure hydrated oxide, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, called **bauxite**.

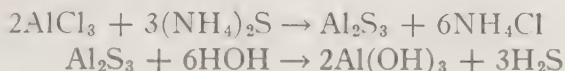
Aluminium hydroxide has been mentioned (Chapter XXI) as an amphoteric hydroxide. As formed by the reaction of a soluble base with an aluminium salt, aluminium hydroxide is a white jelly-like precipitate. Aluminium hydroxide reacts with an acid according to the reaction:



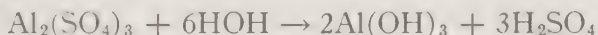
Aluminic acid (ortho), H_3AlO_3 , may lose one molecule of water to form metaluminic acid. By reaction with a base, sodium metaaluminate is formed as follows:



Hydrolysis is a characteristic reaction of aluminium salts. The reaction of ammonium sulphide or ammonium carbonate with an aluminium salt produces a white precipitate of aluminium hydroxide (not aluminium sulphide or aluminium carbonate), as shown by the following reactions using aluminium chloride with ammonium sulphide:



Aluminium salts have important uses as the acid-reacting substance of certain baking-powders (Chapter XXXII), as a clarifying substance in the treatment of water (Chapter XXXIII), and as a mordant in dyeing textiles (Chapter XXXIV). The usefulness of aluminium salts for these purposes depends upon the property of hydrolysis, as shown by the reaction:



Full description of these uses of aluminium salts is given in the chapters mentioned.

While aluminium salts alone are difficult to purify in forming well-defined crystals, a double salt known as **alum** takes a beautiful crystalline shape. Alum, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, is formed when a hot mixture in molecular proportions of potassium sulphate and aluminium sulphate is allowed to cool. The word "alum" may be used also as a general term applied to many compounds containing a sulphate of a monovalent metal, a sulphate of a trivalent metal with the corresponding amount of water, and having a definite crystal structure. Examples are potassium chrome alum, $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$; rubidium alum, $\text{Rb}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$; or ammonium ferric alum, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$.

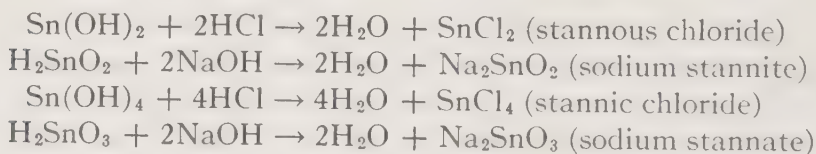
TIN AND LEAD, GROUP IV

Properties and Uses of the Metals. — Tin and lead were known to the people of ancient time and were used for the same purposes for which we use the metals to-day: tin for baking utensils, pipes, sheets, and foil; and lead mainly for water pipes and

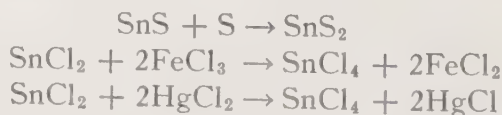
similar equipment. Tin is soft, lustrous, and malleable, while lead is very soft and has little tensile strength. Both metals react only slowly with dilute acids by displacement. With concentrated oxidizing acids, oxidation-reduction reactions occur. Tin plate (steel sheets coated with tin) is quite resistant to the action of the fruit acids, and to bases. Heavy tin plate is quite durable and useful for making many types of containers and kitchen utensils. The slight reactivity of lead toward acid makes it useful for the lining of chemical equipment. Since compounds of lead are poisonous, the use of lead in kitchen utensils and in water pipes is dangerous. When water contains an appreciable amount of carbon dioxide in solution, it may dissolve lead from water pipes and make the water unsafe for drinking. Both tin and lead are important in the preparation of many alloys (Chapter XXVI).

Important Compounds. — Tin and lead each form two ions — stannous, Sn^{++} , and stannic, Sn^{++} , and plumbous, Pb^{++} , and plumbic, Pb^{++} . Both stannous chloride, SnCl_2 , and stannic chloride, SnCl_4 , are used as mordants in dyeing fabrics in the same way that aluminium salts are used (Chapter XXXIV). Some silks contain a very high percentage of tin (or iron) compounds, often over 50 per cent, incorporated with the fiber, to give apparent weight and body to the silk.

Stannous hydroxide and stannic hydroxide are both amphoteric; consequently the following reactions take place:



Since Sn^{++} (stannous ion) readily gives electrons to form Sn^{++} (stannic ion), stannous salts are good reducing agents, as shown by the following equations:



Several oxides of lead are known — lead oxide, PbO , used in making a hard glass; red lead, Pb_3O_4 , a red paint pigment; and lead dioxide, PbO_2 , an oxidizing agent. Basic lead carbonate, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, is an important white paint pigment (previously mentioned). Lead salts are poisonous; hence precautions are necessary for those who work with them in paints. Ethyl gasoline is poisonous because it contains a lead compound (lead tetraethyl).

CHROMIUM, GROUP VI — MANGANESE, GROUP VII

Properties and Uses of the Metals. — Although chromium and manganese are in different groups, their properties are somewhat alike. Chromium is a lustrous metal, very hard and durable, and does not tarnish in oxygen; chromium takes a high polish and is coveted for trays, pitchers, and as a plating on electric toasters and similar equipment. Again, the ornamental parts of automobiles and trains may be chromium plate. While the pure metal reacts by displacement with dilute acids, alloys containing chromium are exceedingly resistant to attack by any acids (even oxidizing acids). Stainless steel, so desirable in cutlery and kitchen utensils, contains 18 per cent chromium. It is exceedingly hard, tough, durable, and resistant to corrosion.

Manganese also is very hard and tough and is only slightly attacked by oxygen. It makes important alloys with iron and other metals. Manganese steel is desirable for tools that must remain hard and strong even when heated by friction or with electricity.

Important Compounds. — The word **chromium** is derived from a Greek word meaning "color." There are three series of chromium salts, each with a characteristic color and corresponding to the valences Cr^{++} , Cr^{+++} , and Cr^{++++} . Chromous salts, Cr^{++} , are blue and are easily oxidized to the chromic salt. Chromic salts, such as CrCl_3 , chromic chloride, and $\text{Cr}_2(\text{SO}_4)_3$, chromic sulphate, are soluble compounds and green in color.

The oxide of chromium in which the valence corresponds to

that given in the periodic table is an acid anhydride. The acid formed when the oxide CrO_3 reacts with water is chromic acid:



Compounds in which chromium has a valence of six are red, orange, or yellow in color. The formulas and names of a few typical compounds are:

K_2CrO_4	potassium chromate, yellow
PbCrO_4	lead chromate, yellow (a yellow paint pigment)
$\text{K}_2\text{Cr}_2\text{O}_7$	potassium dichromate, orange (similar to a pyro salt)
$\text{Na}_2\text{Cr}_2\text{O}_7$	sodium dichromate, orange (used in the tanning of hides)

Because of the variable valence of chromium, it undergoes important oxidation-reduction reactions. Chromates and dichromates are important oxidizing agents, both commercially and in quantitative chemical analysis; as an oxidizing agent Cr^{+++} takes electrons to form Cr^{++} as shown by the following oxidation-reduction reaction:



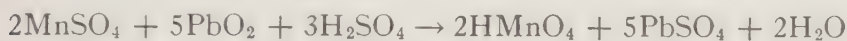
The progress of the reaction of potassium dichromate with a reducing agent may be followed by the color change from orange (Cr^{+++}) to green (Cr^{++}).

Manganese Compounds. — In compounds, manganese shows valences as follows: Mn^{++} , Mn^{+++} , Mn^{++} , Mn^{+++} , and Mn^{++++} . Manganous salts, such as MnS , MnCl_2 , and MnSO_4 , have a pale pink color. Manganese dioxide is important as a catalyst in the preparation of oxygen (Chapter IV), and also as an oxidizing agent in the preparation of the halogens (Chapter XXII). There are compounds corresponding to two acid anhydrides of manganese, MnO_3 and Mn_2O_7 , and their acids, manganic acid, H_2MnO_4 and permanganic acid, HMnO_4 . In permanganic acid, analogous to perchloric acid and perbromic acid, manganese shows the valence indicated by the periodic table. Permanganic acid and permanganates are purple in color.

Because of the variable valence of manganese, it undergoes important oxidation-reduction reactions. Potassium permanganate is an oxidizing agent because manganese Mn^{+++} in acid solution takes electrons to form manganous salts, Mn^{++} . The color change (purple to colorless) in such reactions indicates when enough of the reducing agent has been added to react with all the permanganate salt. Such reactions are important in quantitative analysis. A typical reaction follows:



Manganous compounds, Mn^{++} , may be oxidized to the permanganate (Mn^{+++}) by reaction with lead dioxide in an acid solution, as shown by the reaction:

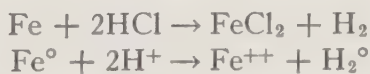


As the reaction proceeds, a purple color is developed as the manganous salt is oxidized to permanganic acid (purple). Since the color of the products formed is characteristic of manganese salts, any of the oxidation-reduction reactions mentioned may be used as a test for manganese ion.

Potassium permanganate is an effective disinfectant and bleaching agent because of its intense oxidizing action.

IRON, COBALT, NICKEL — GROUP VIII

Properties and Uses of the Metals. — In the periodic table, at the middle of the first long series, iron, cobalt, and nickel follow manganese. The elements are much alike in properties. Pure iron is much too soft to be useful, but, with other metals, it forms many alloys or steels which have countless uses varying from the making of nails and pins to the building of bridges and skyscrapers. Iron oxidizes (rusts) readily especially in moist air, and the oxide (unlike those of zinc and aluminium) is loose and falls away from the metal and leaves a surface exposed to further oxidation. The metal readily reacts by displacement with dilute acids:



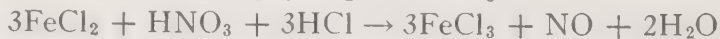
Although iron utensils are heavy and are corroded by oxygen and

by fruit acids, they have always been used more or less for certain types of kitchen equipment. However, there is a vast difference between the crude iron pots and kettles of New England days and the streamlined stainless steel utensils of to-day for which chemical research is largely responsible.

Nickel and cobalt are most important as alloys. A cobalt-aluminium alloy is especially hard and strong. Monel metal is made from a natural ore which contains approximately 66 per cent nickel and 33 per cent copper. Monel metal is desirable for table-tops, utensils, and counters which have to be kept clean and bright, even after contact with fruit and vegetable acids, and steam. A well-known restaurant in this country equips all the kitchens with copper kettles having a nickel lining. The copper furnishes high heat conductivity, and the lining made of nickel is strong, durable, and stainless.

Important Compounds. — Iron forms two ions, ferrous, Fe^{++} , and ferric, Fe^{+++} . Ferrous salts are pale green or almost colorless in solution and ferric salts are yellow. Ferrous sulphate (like aluminium and stannous salts) acts as a mordant in dyeing textiles and in giving luster and weight to silk fabrics. It may also be used like aluminium salts in the clarification of turbid water (Chapter XXXIII). Prussian blue or ferric ferrocyanide, $\text{Fe}_4(\text{FeC}_6\text{N}_6)_3$, is a blue pigment known as "blueing" in the laundry. (See test for ferric ion, Chapter XXVII.)

Since ferrous ion loses electrons to form ferric ion, ferrous salts are reducing agents, as shown by the following oxidation-reduction reactions:



Likewise, ferric salts may be considered as oxidizing agents in reactions in which ferric ion is reduced to ferrous ion, as in



It is important that we consider the iron content of our foods, because iron is one of the building materials for the hemoglobin of the blood.

Nickel forms nickel ion, Ni^{++} , and the usual cobalt salt is cobaltous, Co^{++} . Cobalt has also a valence of positive three. Nickel salts are green in solution; cobalt salts are red or pink in solution, although the anhydrous salt is deep blue. Cobalt compounds are fused with glass to give it a blue color.

THE COPPER FAMILY, GROUP I — COPPER, SILVER, GOLD

Properties and Uses of the Metals. — Although in every group the two families of elements have different chemical and physical properties, in Group I this difference is especially noticeable. In sharp contrast to the high reactivity of the alkali metals, copper, silver, and gold may be characterized as a "lazy" family with little tendency to react either with air and moisture or with any of the ordinary laboratory reagents. Silver and gold are classed with the noble metals because of their resistance to chemical reactions. While the alkali metals are found at the head of the electrochemical series, these three metals are at the end of the series. They have the physical properties of metals useful in the industries. Copper is tenacious and a good conductor of electricity, which makes it desirable for electric wiring. The properties of silver and gold, malleability, luster, and color, make them valuable for coinage, ornaments, and tableware. Probably the most valuable property of these metals is their chemical inactivity or resistance to oxidation. Articles made from them preserve their usefulness and appearance longer than they would if made from less resistant metals.

Copper, silver, and gold are below hydrogen in the electrochemical series. They will not displace hydrogen from dilute acids and can be dissolved only with oxidizing acids. Copper and silver are oxidized by nitric acid, while gold can be oxidized only with aqua regia, a mixture of nitric and hydrochloric acids (Chapter XIX).

Important Compounds. — Copper forms two ions, cuprous, Cu^+ , and cupric, Cu^{++} . One of the most familiar compounds is

blue vitriol, or hydrated copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; from this compound, other copper salts are made. Copper salts are poisonous, and hence many fungicides and insecticides contain them. A mixture of copper sulphate and calcium hydroxide (containing precipitated basic copper sulphate) is satisfactory for fruit trees. Paris green, a mixture of copper acetate and copper arsenite, $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Cu}_3(\text{AsO}_3)_2$, is another insecticide.

The serious disadvantage in the use of copper or its alloys in cooking utensils is the poisonous property of the salts of copper. Although copper is below hydrogen in the electrochemical series and does not react with dilute acids, it reacts with organic acids in the presence of air to form copper salts. The basic copper acetate, known as verdigris, is often formed in this way. Because of these poisonous salts, the use of copper in any alloy that comes in contact with food may be dangerous. Although copper salts are poisonous, minute traces of copper ion are important in nutrition.

A most characteristic property of silver salts is their instability to light. A photograph film consists of silver bromide, AgBr , or silver iodide, AgI , in a gelatin base. During the instant that the film is exposed to light, the silver salt undergoes some decomposition. This is further reduced by the developer, and forms a dark deposit of silver where the strongest light touched the film. Where the unchanged silver salt is washed out, the film is clear. The entire art of photography (hence the moving picture industry) depends on simple chemical changes which take place with silver salts. Silver nitrate and possibly other silver salts have a cauterizing effect and thus are important for medical purposes.

Gold forms aurous ion, Au^+ , and auric ion, Au^{+++} . They are of interest because of the ease with which they may be reduced to metallic gold.

THE PLATINUM FAMILY. RUTHENIUM, RHODIUM, AND PALLADIUM: OSMIUM, IRIDIUM, AND PLATINUM

These two groups of metals, triads of the periodic table (Group VIII), are known as "precious metals." They have so little chemical reactivity and are so malleable and brilliant when polished

that they are highly desirable for jewelry. The resistance to corrosion and high melting-point of platinum and iridium make them valuable in the manufacture of certain types of scientific equipment.

QUESTIONS AND PROBLEMS

1. To illustrate the reactions characteristic of the alkali and alkaline earth metals, write equations for the reaction of oxygen with potassium, caesium, and barium; for the reaction of water with rubidium and calcium.
2. Fill in the blanks of the following table:

<i>Compound</i>	<i>Formula</i>	<i>Chemical Name</i>	<i>Source</i>	<i>Use</i>
Salt				
Washing-Soda				
Baking-Soda				
Glauber's Salt				
Borax				
Lye				
Saltpeter				
Chile Saltpeter				
Water-Glass				

3. Name five forms in which calcium carbonate occurs in nature. Give names and formulas for four other naturally occurring compounds of calcium.
4. Write equations to show the preparation of quicklime from calcium carbonate; of slaked lime from quicklime; of bleaching-powder from quicklime.
5. Write the formula and state a commercial use of each of the following: strontium hydroxide, barium sulphate, magnesium (metal), magnesium hydroxide, magnesium oxide, zinc sulphide, cadmium sulphide, mercurous chloride, mercuric chloride.
6. State the properties of each of the elements of the magnesium family that make them valuable as metals.

TABLE XXI

SOURCE OF THE METALS

<i>Metal</i>	<i>Compound Used as Source</i>	<i>Source</i>	<i>Preparation of Metal</i>
Sodium	NaCl	Salt mines, Ocean	Electrolysis of fused chloride
Potassium	KCl, MgCl ₂ , KCl	Germany, New Mexico	Electrolysis of fused chloride
Lithium	Complex Silicates	South Dakota, New Mexico, California	Electrolysis of fused chloride
Rubidium	Complex Compounds		Electrolysis of fused cyanide
Cæsium	By-product from Lithium ore	South Dakota and Maine	Electrolysis of fused cyanide
Calcium	CaCO ₃ , CaSO ₄	Widespread	Electrolysis of fused chloride
Strontium	SrSO ₄ , SrCO ₃	Widespread	Electrolysis of fused chloride
Barium	BaSO ₄ , BaCO ₃	Missouri, Georgia, California, Tennessee	Electrolysis of fused chloride
Magnesium	MgCO ₃ , CaCO ₃ , MgBr ₂ KCl, MgCl ₂ , MgSO ₄	Western U. S., Michigan	Electrolysis of fused chloride
Beryllium	Complex silicates	South Dakota	Electrolysis of fused chloride
Zinc	ZnS, ZnCO ₃ , Zn(FeO ₂) ₂	Missouri, Kansas, New Jersey, Oklahoma	Roasting; reduction with carbon; electrolysis
Cadmium	By-product of zinc ores	New Jersey, Montana	Reduced with C
Mercury	Native, mixed with silver and gold, or as sulphide	California and Texas	Roasting and distilling
Aluminium	Impure oxide	Arkansas and Southern U. S.	Electrolysis of oxide in fused cryolite
Tin	Oxide	England, Bolivia, China	Roasting and reduction
Lead	Sulphide	Missouri, Oklahoma	Roasting and reduction
Titanium	Oxide	Idaho, Utah Virginia	Reduction with aluminium or electrolysis

Germanium	Oxide in silver ore	South Africa	Reduction with carbon
Zirconium	Silicates	Wales, Russia	Reduction with aluminium
Vanadium	$\text{Pb}(\text{VO}_3)_2$	Peru	Reduction of chloride with hydrogen
Columbium	K_2CbF_7	Nigeria, Western U. S.	Reduction with zinc, and electrolysis
Tantalum	$\text{K}_2\text{TaF}_7, \text{FeTa}_2\text{O}_6$	Australia, Western U. S.	Reduction with hydrogen
Antimony	Sulphide	China, Bolivia, Mexico	Roasting and reduction with carbon
Bismuth	Sulphide	United States, Bolivia, Canada	Roasting and reduction with carbon
Chromium	$\text{FeO.Cr}_2\text{O}_3$	Africa, Cuba, New Caledonia	Reduction with aluminium
Tungsten	FeWO_4	United States, China, Bolivia, Mexico	Reduction with carbon, hydrogen
Molybdenum	$\text{MoS}_2, \text{PbMoO}_4$	Colorado, Arizona	Reduction with carbon
Manganese	MnO_2	Russia, Africa, Brazil. Low grade in United States	Reduction with aluminium
Iron	$\text{Fe}_2\text{O}_3, \text{Fe}_3\text{O}_4$	Minnesota	Reduction with carbon
Cobalt	$\text{CoAs}_2, \text{CoAsS}$	Canada	By-product of silver mines
Nickel	Sulphide	Canada, Norway	Reduction with carbon
Copper	Native and $\text{Cu}_2\text{S}, \text{CuFeS}_2$	Western U. S., Alaska	Roasting the ore. Electrolysis in water solution
Silver	Native and as $\text{Ag}_2\text{S}, \text{AgCl}$	Western U. S., Mexico	Alloyed with mercury. Combined with potassium cyanide. Purified by electrolysis
Gold	Native	Western U. S., Alaska	
Platinum Metals	Native	Russia, Colombia, Alaska, Oregon	

7. Write equations for the reaction of:
- (1) milk of magnesia with hydrochloric acid
 - (2) baking-soda with vinegar
 - (3) saltpeter with sulphuric acid
 - (4) hydrolysis of borax; of washing-soda; of water-glass
 - (5) electrolysis of melted lye
 - (6) limestone with hydrochloric acid
 - (7) quicklime with water
 - (8) zinc with steam
 - (9) zinc with lye
 - (10) zinc with vinegar.
8. Write equations to show the reaction of each of the following amphoteric hydroxides with sulphuric acid and with sodium hydroxide; name each of the salts formed:
- | | |
|--------------------|-----------------------|
| zinc hydroxide | antimonious hydroxide |
| stannous hydroxide | plumbous hydroxide |
| stannic hydroxide | |
9. Write equations to show the reaction of lye with aluminium and with aluminium oxide. Why does aluminium turn dark when in contact with alkaline solutions?
10. Give the formula for alum. Explain the meaning of the term "an alum" and illustrate with two formulas.
11. Write the equation to show the hydrolysis of aluminium sulphate. Briefly tell of the uses of aluminium salts which depend on the property of hydrolysis.
12. Give the commercial uses of the following metals: tin, lead, chromium, manganese, iron, nickel, copper, silver, gold, and platinum.
13. Give the name and the commercial use of the following: Pb_3O_4 ; $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$; KMnO_4 ; $\text{Fe}_4(\text{FeC}_6\text{N}_6)_3$; $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; AgBr ; AgNO_3 .
14. What is the physiological importance of compounds of iron, tin, lead, and copper?
15. Balance the following oxidation-reduction reactions and tell what is observed when each occurs:
- $$\text{K}_2\text{Cr}_2\text{O}_7 + \text{FeCl}_2 + \text{HCl} \rightarrow \text{CrCl}_3 + \text{FeCl}_3 + \text{KCl} + \text{H}_2\text{O}$$
- $$\text{K}_2\text{Cr}_2\text{O}_7 + \text{KI} + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \text{I}_2 + \text{H}_2\text{O}$$
- $$\text{KMnO}_4 + \text{FeSO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{MnSO}_4 + \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$$
- $$\text{MnSO}_4 + \text{PbO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{HMnO}_4 + \text{PbSO}_4 + \text{H}_2\text{O}$$
- $$\text{FeCl}_2 + \text{HNO}_3 + \text{HCl} \rightarrow \text{FeCl}_3 + \text{NO} + \text{H}_2\text{O}$$
- $$\text{KMnO}_4 + \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_4 + \text{MnSO}_4 + \text{H}_2\text{SO}_4$$
16. Write formulas and names of compounds showing two different valences of each of the following: copper, mercury, lead, iron, cobalt, chromium, and manganese.

17. Write formulas for:

cuprous chloride	plumbic chloride
mercuric oxide	plumbic oxide
mercurous chloride	potassium permanganate
plumbous chloride	sodium dichromate
plumbous oxide	chromic acid
auric (gold) chloride	sodium metaluminate
sodium stannate	ferrous sulphate
sodium stannite	ferric sulphate
permanganic acid	chromic chloride
manganous sulphate	stannic sulphide

18. Devise methods for the preparation of the following: copper nitrate from copper; sodium hypochlorite from sodium hydroxide; calcium chloride from lime; potassium sulphate from potassium chloride; ferric chloride from ferric oxide; magnesium nitrate from magnesium carbonate.
19. Write equations for the reaction of concentrated nitric acid with mercury; concentrated sulphuric acid with silver; aqua regia with gold.

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CHAPTER XXVI

THE ALLOYS OF METALS

Introduction. — The chemistry of the most familiar metals involves primarily a study of the properties that make them resistant to wear and corrosion. Iron, one of the most abundant of the metals, becomes corroded so easily that it must be protected with paint or enamel or mixed with other elements to increase its resistance to corrosion. Silver articles need constant care because of the tarnish which forms on the surface. On the other hand, gold and platinum jewelry always remain bright, and chromium-plated tea-sets and automobile fixtures seldom become tarnished. As we study the metals, it is surprising to find how few of them are used in the form of the pure element. The chemist and the metallurgist have learned to mix metals in different proportions to produce metal mixtures, known as **alloys**, which have properties quite different from those of the original metals. Sometimes a trace of some rare and expensive metal is added to a metal abundant in nature to form an alloy; again, two familiar and abundant metals may be mixed in almost equal parts. A result of this important work of mixing metals is that to-day we have a variety of alloys that may be adapted to almost every desired use.

The structure of an alloy depends on the chemical and physical properties of the constituents and on the method used in cooling the melted mixture to the temperature of solidification and below this temperature. When two metals are melted, they may combine in a definite proportion to form a chemical compound. The following compounds have been shown to be present in alloys: Cu_2Zn_3 , CuZn_6 , CuAl_2 . In some alloys a metal is combined with a small amount of a non-metal, such as phosphorus or carbon. Sometimes metals solidify in a solid solution or a homogeneous mixture. Copper and nickel will form a solid solution when they are melted together and then solidified. In many cases, however,

the metals do not solidify as a true solution. Instead, the particles or grains of each metal solidify separately in a fine mixture. When the metals form a compound, one metal is usually present in excess. As the mixture cools, the compound may either dissolve and form a solid solution with the uncombined metal, or it may be mixed with the metal in relatively coarse grains. Each of these conditions affects the properties of the alloy.

In many cases, one component of a molten mixture of metals begins to precipitate while the other component is still in solution. When the entire mixture freezes or solidifies, the precipitate first formed will be present in larger grains dispersed throughout the solid mixture. This type of alloy formation may be compared with the freezing of a saturated solution of salt. As the solution is cooled to a low temperature, it becomes supersaturated and the excess salt precipitates, while the solution remains saturated at the lower temperature. The solution does not freeze until it has been cooled to -22.4°C . At this temperature the salt and water both freeze, with the first precipitate of salt scattered in relatively large grains throughout the frozen mixture. A similar process may have been noted in certain ice-creams that give a sensation of being sandy, due to particles of milk-sugar that precipitate in large particles before the custard begins to freeze.

Alloys of lead and antimony often form as mixtures of the type just described. When equal parts of these two metals are melted together at 500°C . or above and then cooled, the antimony is the first to crystallize or precipitate. When the alloy has cooled to near 250°C ., six sevenths of the antimony has precipitated. At this temperature (as at -22.4°C . for the salt solution) both metals precipitate as fine granules. The coarser granules of the antimony that were first precipitated are dispersed throughout the mixture. The temperature at which the two metals solidify remains constant until all of it has frozen. This temperature is known as the **eutectic point**. The mixture that forms has a constant composition and is called the **eutectic mixture**. When a mixture of metals like the one just mentioned is cooled suddenly to a temperature below the eutectic point, the crystals of either constituent may be prevented from forming separately. Instead,

they may precipitate as a fine-grained mixture. An alloy of this structure may be harder and less brittle than one containing the coarser granules.

The size of the crystals and the structure of an alloy may be determined by the use of photomicrographs. A section of the polished alloy is etched with acid and a photograph is made of the surface, enlarged from 500 to 1,000 times. When an acid is used that attacks only one of the constituents, the size and form of the crystals of precipitated metal may be distinguished. An experienced metallurgist can estimate from such a photograph the strength and durability that may be expected from the alloy. Recently X-rays have been used in the study of alloys. The arrangement of the atoms in the crystals of the alloy may be determined through a study of the diffraction of the X-rays.

Properties of Alloys. — The properties of an alloy differ from those of the components just as the properties of a solution or of a compound differ from those of the constituents. Some of the important properties are as follows:

1. The melting-point of an alloy (a solid solution) is usually lower than that of either constituent. This condition is comparable to that of solutions having a lower freezing-point than the pure solvent. A frozen sugar solution will melt at a lower temperature than either sugar or water. We may expect, then, that a solid solution of two metals will melt at a lower temperature than will either component in the pure state. This fact is of importance in preparing the low-melting alloys used in fuse plugs, in solder, and in automatic water-sprinklers and fire-extinguishers.

2. The density of an alloy is not usually the average of the density of the two metals. This indicates that molecules of different kinds may fit more closely or more loosely than molecules of one kind.

3. The resistance of an alloy to scratching or penetration and the tensile strength of an alloy depend on two factors: the method of preparing the alloy and the kind of metals that are constituents of the alloy. A solid solution or a mixture of fine crystals usually

has a greater tensile strength than an alloy in which large crystals have grown.

4. The casting capacity of an alloy is important. Kettles and frying-pans, as well as other heavy metal pieces, are cast by pouring the melted alloy into a mold. An alloy that is suitable for casting should melt at a comparatively low temperature and form a thin liquid that pours easily. Moreover, it should not change greatly in volume during solidification. An alloy that expands slightly when it solidifies fills the crevices of the mold and so the cast has a sharp, distinct outline. Type-metal, an alloy of antimony, lead, and tin, has the property of expanding when it solidifies, and so it is useful in making well-defined impressions of the type.

5. The color of an alloy may be different from that of any of the constituents. This makes it possible to prepare gray, green, and white (alloyed) gold.

6. Alloys may be made that are more resistant to chemical influence than the constituent metals. Pure metals differ in the type of corrosion to which they are susceptible. Some metals are resistant to the action of acids, while others are attacked by acids but are resistant to the action of bases. A few metals, resistant to the action of strong inorganic acids, are attacked by weak organic acids. The corrosive properties of the metals may not be apparent in the alloys of the metals; hence valuable alloys may be made which are more resistant to corrosion by acids and by bases and also by moisture and the atmosphere than the constituent metals.

Kinds of Alloys. — Alloys may be classified according to the most familiar metal constituent. The alloys in common use are usually formed from the metallic elements, copper, lead, aluminum, iron, nickel, tin, zinc, gold, and silver. The approximate percentage composition of some alloys is given at the close of this chapter.

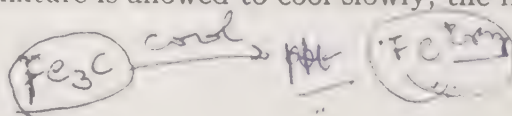
Copper alloys have been known and used since early historic times, and they are still important. Alloys of copper with 18 to 40 per cent of zinc are known as **brass**. Brass has good casting

properties and is highly resistant to corrosion. The alloy **bronze** is made by adding zinc and tin to copper. It is an extremely hard and non-corroding alloy. Brass is yellow in color, and bronze is brown. Small amounts of copper are added to gold and silver to make a hard and durable alloy which is used for coins, tableware, and jewelry.

One of the most interesting alloys of copper in use to-day is **monel metal**, made from an ore that contains copper and nickel. When this ore is reduced, the two metals solidify in a solid solution to form an alloy that is as heavy as steel and especially resistant to corrosion. The large cooking utensils used in restaurants and hospitals are sometimes made of monel metal. It is expensive but has many properties that make it quite satisfactory for this purpose. Stainless steels are less expensive and have replaced monel metal for many types of utensils.

Iron Alloys. — Iron forms many useful alloys. Carbon, silicon, and phosphorus, as well as many metals, may be incorporated with iron to give products with widely different properties. Heat treatment also has an influence upon iron alloys. When iron is prepared from the oxide, Fe_2O_3 , by reduction with coke, some of the carbon combines with the iron, forming iron carbide Fe_3C . This crystallizes after the melted iron solidifies and produces a hard, brittle metal with a low melting-point. This is known as **cast-iron** and has many uses, such as in the manufacture of stoves, sewing-machines, and washing-machines. It is an inexpensive form of iron, but its weight, brittleness, and tendency to corrosion make it undesirable for many purposes. Cast-iron may be given a treatment which removes the silicon and phosphorus and most of the carbon. The product, which is known as **wrought-iron**, is approximately 99.8 per cent pure. Wrought-iron is fibrous and tough and is easily molded when heated. It is used for chains, bolts, wire, and decorative work such as lamps and fixtures.

Steel, the most useful form of iron, is an alloy of iron with 2 per cent or less of carbon as iron carbides. The process used in the manufacture of steel determines, in a measure, its properties. When the molten mixture is allowed to cool slowly, the iron car-



bide precipitates and the iron crystallizes in an allotropic form that is stable at low temperatures. This steel is soft and pliable; however, the hard crystals of iron carbide that are mixed with it make the steel more resistant to wear than wrought-iron. When red-hot steel with iron carbide in solid solution is cooled quickly, the iron crystallizes in a form that is stable at high temperatures (with iron carbide still in true solution). This steel is hard and brittle. By reheating this brittle steel to a definite temperature to allow some crystals to change to the other allotropic form, the steel may be given any degree of hardness desired. This process is known as **tempering steel**.

The various products obtained by making alloys of steel and other metals have characteristic individual properties. The addition of 2 to 4 per cent of nickel produces a tough non-corrosive steel used for armor-plate, engines, and automobile parts. The addition of 11 to 14 per cent of manganese gives a hard, tough, non-magnetic steel for railroad rails and steam-shovels. An alloy of vanadium results in a tough, ductile steel used for automobile springs; tungsten gives a sharp cutting edge that is not destroyed by the temperature attained with high-speed tools. The **stainless steels** are among the most interesting alloys found in the home. They are used in making cutlery, stoves, cooking utensils, plumbing fixtures, and refrigerators. Such steels contain from 10 to 20 per cent of chromium and a smaller percentage of nickel or cobalt. By varying the carbon content and by tempering these steels, they may be made hard or soft and tough or brittle as desired.

Steel is often protected by a coating of some non-corroding substance; iron bridges are painted to prevent them from rusting, and iron cooking utensils are covered with enamel. Iron may be protected by covering it with other metals that are less subject to corrosion, such as nickel, silver, tin, and copper. Nickel-plating is often used on small articles made of steel. Silver, plated over iron, is used for tableware. Iron wires may be covered with copper. Iron dipped in molten tin makes a material useful for the familiar "tin" can in which food is preserved.

Silver and copper are below iron in the electrochemical series and are therefore less active than iron. When the plating of these metals wears off and the iron is exposed, acids and corrosive agents react with the more active iron. Moreover, the corrosion is especially rapid because an electric

cell may form between the two metals. This causes the more active element to dissolve rapidly. Aluminium, zinc, and chromium are above iron in the electrochemical series. When iron is plated with any of these metals, the iron will not be attacked by acids until the more active elements have been entirely dissolved. Although these metals are high in the electrochemical series, they are not easily corroded because their oxides adhere to the metal surface and protect it against chemical action. Aluminium and chromium plating is rapidly being developed. Iron coated with zinc, known as galvanized iron, has been used for roofs, sinks, and other purposes.

Other Alloys. — Low-melting alloys, used in fuse plugs, solder, and automatic fire extinguishers are made by mixing two or more low-melting metals. A typical alloy of this type is Wood's metal, which is composed of bismuth, lead, tin, and cadmium; it melts at 70° C. (below the boiling-point of water).

Nichrome, an alloy containing nickel and chromium and sometimes iron, has a high melting-point; for this reason it is used in making the heating units of electrical apparatus.

Because pure gold is too soft to be used for jewelry, coins, or tableware, it is usually alloyed with copper or a mixture of copper and silver. The amount of gold present in such an alloy is usually stated in terms of carats. In this system, 24 carat gold represents 100 per cent gold, while 18 carat gold contains 18/24 or 75 per cent of the element.

An alloy of platinum with iridium has a faint blue color and is one of the strongest alloys known. These properties make it useful in jewelry for slender chains.

Aluminium is alloyed with copper to make it harder, and with other light metals to make a light-weight alloy for use in airplanes, dirigibles, and streamlined trains.

In equipping a kitchen, it is often necessary to choose between aluminium metal, monel metal, stainless steel, or enameled ware. In choosing jewelry, we decide among gold, platinum, or less expensive alloys. Light fixtures, bathroom fixtures, and some furniture may be obtained in a variety of metals. It is pointed out in this chapter that utensils are seldom made of a pure metal, but almost always of alloys. Thus we are making a choice between

alloys with properties quite different from those of the pure metals.

APPROXIMATE PERCENTAGE COMPOSITION OF SOME ALLOYS

Duralumin.....	Al 95; Cu 3; Mn 1; Mg 0.5
Magnalium.....	Al 90-94; Mg 2-10
Aluminium bronze.....	Al 2-10; Cu 90-98
Brass.....	Cu 60-80; Zn 20-40
Bronze.....	Cu 70-95; Sn 1-18; Zn 0-2
Monel metal.....	Cu 27; Ni 68; Mn and Fe 5
White gold.....	Au 90; Pd 10
Green gold.....	Au 60; Ag 35; Cu 5
Gray gold.....	Au 20; Pd 80
18-carat gold.....	Au 75; Cu and Ag 25
Gold coin.....	Au 90; Cu 10
Nickel coin.....	Cu 75; Ni 25
Nichrome.....	Ni 60-80; Cr 11-20; Fe 0-25
Silver coin.....	Ag 90; Cu 10
Sterling silver.....	Ag 90; Cu 10
Stainless steel.....	Cr 18; Fe 74; Ni or Co 8
Wood's metal.....	Bi 50; Pb 25; Sn 12.5; Cd 12.5
Pewter.....	Sn 85; Cu 7; Bi 6; Sb 2
Type metal.....	Pb 82; Sb 15; Sn 3
Solder.....	Sn 60-70; Pb 35-45

QUESTIONS AND PROBLEMS

1. Give three types of structure that alloys of metals may form.
2. Give the meaning of the terms: alloy, eutectic mixture, solid solution, photomicrograph.
3. Give six ways in which an alloy may differ from its constituents. How does the melting-point usually differ? Give the uses of low-melting alloys.
4. Give names, properties, and uses of three copper alloys and of three gold alloys.
5. Compare the composition, properties, and uses of steel, cast-iron, and wrought-iron. What is tempered steel? Give four ways of preventing iron from rusting.
6. Give uses and approximate composition of Wood's metal, monel metal, type metal, stainless steel, galvanized iron, silver plate, platinum.

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CHAPTER XXVII

ANALYTICAL CHEMISTRY

ONE of the most important applications of chemistry is the identification of the elements of which substances are composed; for example, we are interested in knowing the elements that make up the human body and we find it necessary to know the composition of our foods in order to keep our bodies supplied with the essential elements. It is the work of special courses in chemistry and foods to discuss all the nutrition requirements, but a few examples will indicate the work of the analytical chemist in this problem: an analysis of bone tissue indicates that calcium and phosphorus are needed to repair and build bone structure in the body — food analysis shows the kind and quantity of foods needed in the diet to meet these requirements. Again, an analysis of blood indicates whether the diet contains sufficient iron to supply the needs of the body.

Under present conditions, many of our foods are prepared by commercial establishments. They are under government supervision and control (Food and Drugs Act of Congress, Revision of 1939). Analytical chemists are essential in both the preparation and control of foods. They determine whether milk contains the required amount of fat, total solids, and other constituents; they determine whether baking-powder forms a certain amount of available carbon dioxide and contains no ingredients harmful to the body; they determine whether fruit and vegetable products contain only the coloring matter and preservatives allowed by the Foods Act; they determine the conditions for cold storage most desirable to preserve the flavor and texture of foods.

The problem of insecticide sprays was mentioned in Chapter XXIII. The practice of spraying vegetables and fruits to destroy insects and larvæ presents the problem of the spray residue left on the food as purchased. It makes necessary the work of an analyt-

ical chemist to determine the arsenic compounds present on the surface of apples or other fruits and the arsenic, lead, or copper ions attached to celery, cauliflower, and other vegetables. In addition it is necessary that he make analyses of prepared fruit and vegetable products.

The requirements for drugs, medicines, and cosmetics (Foods and Drugs Act, 1939) also makes the work of the chemist essential in the analysis of these products.

A brief reference should be made to the work of the analytical chemist in the textile industry. The manufacturer of textiles must know the composition of preparations used to bleach the undesirable coloring matter of natural fibers, and of substances used to separate the fiber from adhering material not wanted in the textile. They must know chemical methods of treatment to enhance the desirability and beauty of the fabric. The firms from which the fabrics are distributed need an analytical chemist to determine whether the fabrics meet certain government specifications; fibers and fabrics made from them are subjected to chemical analysis to determine the kind and amount of salts impregnated in the fiber and to determine the effect of the compounds on the durability of the textile.

These few illustrations serve to show the importance of the analytical chemist in industry and to problems of specific interest in the home. Because there are so many applications of analytical methods, the student should become familiar with the means of testing for the ions that may be encountered: In body tissues and fluids — calcium, iron, potassium, sodium, magnesium, and phosphate; substances added to foods for preservative action such as borates and sulphites; ions present in foods because of insecticide sprays and metal containers, such as copper, lead, mercury, and arsenic. To understand the reactions of baking-powders (Chapter XXXII) we will need to include tests for sodium, potassium, aluminium, carbonate, sulphate, phosphate, and tartrate ions. The problems involved in hard and soft water (Chapter XXXIII) will require tests for sodium, calcium, magnesium, and iron salts and for carbonate, sulphate, and chloride ions; washing-powders and water-softeners will require a study of borate and phosphate

ions. In the study of textiles (Chapter XXXIV), we will be interested in many of the ions just mentioned and in addition, sulphites and other bleaching compounds, salts used as dyes, and stannous, chromium, and aluminium salts used in the dyeing, weighting, and finishing of textiles.

The following tabulation is a summary of the characteristic reactions used as tests for some of the most familiar of these ions. They include ionic or complete equations for most of the tests. Some of the tests have been given in previous chapters and are reviewed to make the summary more complete.

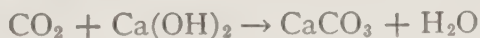
This tabulation is not a substitute for laboratory directions. The essential details for carrying out the tests and the conditions for elimination of interfering reactions are a part of the laboratory procedures and are not included in this discussion.

TESTS FOR NEGATIVE IONS

Carbonate Ion. — The addition of hydrochloric acid to a carbonate gives an effervescence with a colorless, odorless gas, carbon dioxide:



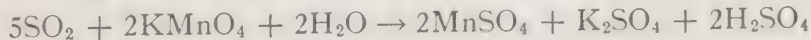
Carbon dioxide gas with lime-water forms a white precipitate, CaCO_3 :



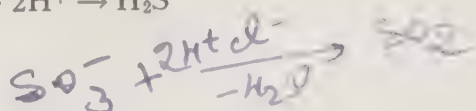
Sulphite Ion. — The addition of hydrochloric acid to a sulphite gives a colorless gas, sulphur dioxide:



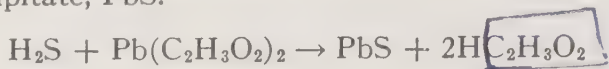
Sulphur dioxide is recognized by the characteristic odor of burning sulphur; also by a test in which potassium permanganate (purple) is reduced to manganous sulphate (colorless):



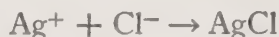
Sulphide Ion. — The addition of hydrochloric acid to a sulphide gives a colorless gas, hydrogen sulphide:



The gas has a disagreeable odor, as of decayed eggs. The reaction of hydrogen sulphide gas with a lead salt (lead acetate) gives a black precipitate, PbS.



Halides. — The addition of silver nitrate to a solution containing chloride ion forms a curd-like white precipitate insoluble in nitric acid.

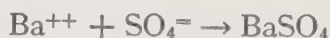


Silver bromide and silver iodide are pale yellow precipitates formed when silver ion is added to bromide and iodide ions. These precipitates are also insoluble in nitric acid.

We may distinguish between bromide and iodide ions by a test which forms the elements; bromine from a bromide gives a brown gas, and iodine from an iodide gives a purple gas. The bromide or iodide is heated with manganese dioxide and concentrated sulphuric acid:



Sulphate Ion. — The addition of barium chloride to a solution of a sulphate gives a white precipitate, insoluble in hydrochloric acid.



Phosphate Ion. — (a) The reaction of magnesia mixture (ammonium chloride, ammonium hydroxide, and magnesium chloride) with a solution containing phosphate ion, forms a white precipitate which dissolves in hydrochloric acid, and again forms a precipitate when the acid is neutralized with ammonium hydroxide:



The reaction is used as a test for phosphate ion with a magnesium salt as the reagent, or for magnesium ion with disodium phosphate as the reagent.

(b) When a solution of ammonium molybdate is heated with a solution containing phosphate ion, a yellow precipitate forms slowly; the yellow compound is a complex ammonium phosphomolybdate.

Nitrate Ion. — When a mixture containing ferrous sulphate and nitrate ion is brought in contact with concentrated sulphuric acid, the brown compound $\text{FeSO}_4 \cdot \text{NO}$ forms at the junction point of the sulphuric acid with the ferrous sulphate-nitrate mixture.

Borate Ion. — A mixture of a borate with concentrated sulphuric acid and methyl alcohol forms methyl borate, which burns with a green flame.

Tartrate Ion. — Tartrates, like other carbon compounds, decompose when heated with concentrated sulphuric acid to form a black residue of carbon. Tartrates give off the odor of burning sugar.

Acetate Ion. — Acetate salts, heated with concentrated sulphuric acid, form acetic acid which may be recognized by its odor. If ethyl alcohol is added to the mixture, a fruity odor of ethyl acetate is evident.

TESTS FOR POSITIVE IONS

Ammonium Ion. — When a solution of an ammonium salt is heated with an excess of a strong base (sodium hydroxide), ammonia gas is evolved:

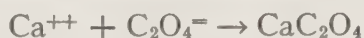


Ammonia gas may be detected by its odor; also, ammonia is the only gas that reacts with the moisture on pink litmus paper to give a base, and changes the pink litmus to blue.

Sodium and Potassium Ions. — Sodium and potassium salts are volatile when heated in a flame and impart characteristic colors to the flame. Sodium ion gives an orange-yellow and lasting

envelope of flame; potassium ion gives a violet color that cannot be seen in the presence of the sodium flame. It may be detected by viewing the flame through blue cobalt glass, which absorbs the yellow color but allows the violet color of the potassium flame to be visible.

Calcium Ion. — Calcium ions give a brick red color to the flame. The reaction of ammonium oxalate with calcium ions in a neutral or weakly acid solution forms a white precipitate of calcium oxalate, CaC_2O_4 , soluble in hydrochloric acid.



Barium Ion. — Barium ions give a green color to the flame. The reaction of potassium dichromate with barium ions in a neutral solution forms barium chromate, BaCrO_4 , a characteristic yellow precipitate.



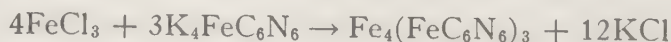
The reaction is used to test for barium ions with potassium dichromate as the reagent, or for chromate ions with barium chloride as the reagent.

Magnesium Ion. — See test for phosphate ion. In another test, magnesium hydroxide is dyed a light blue color with paranitrobenzene azoresorcinol (magnesium reagent) in an alkaline, NaOH , solution.

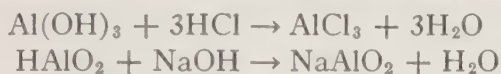
Ferric and Ferrous Ions. — For a satisfactory test, ferrous ions should be oxidized to ferric ions, as shown by the equation:



With a solution of ferric chloride, a soluble base forms a gelatinous rust-colored precipitate of ferric hydroxide, soluble in hydrochloric acid. The reaction of ferric ion with potassium ferrocyanide forms ferric ferrocyanide, a dark blue salt:

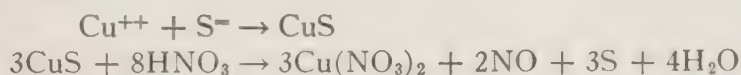


Aluminium Ion. — The reaction of aluminium ions with ammonium hydroxide forms a white gelatinous precipitate of aluminium hydroxide, $\text{Al}(\text{OH})_3$, soluble in hydrochloric acid and in a strong base, because of its amphoteric properties (Chapter XXV):

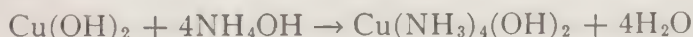


To give a characteristic test for aluminium ion, a dye may be used in a solution containing an aluminium salt with ammonium hydroxide; the precipitate of aluminium hydroxide is dyed with the dye aluminon, to form a characteristic red compound.

Cupric Ion. — The reaction of cupric ions with hydrogen sulphide forms a black precipitate, cupric sulphide, CuS , soluble in nitric acid:

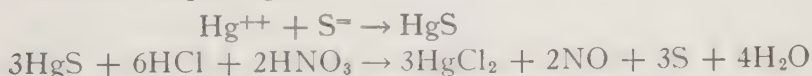


Copper compounds react with excess of ammonium hydroxide to form a deep blue solution containing a complex cuprammono ion, $\text{Cu}(\text{NH}_3)_4^{++}$:

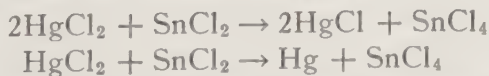


Mercurous and Mercuric Ions. — Mercurous chloride HgCl , a white insoluble compound, reacts with ammonium hydroxide to form a gray to black deposit ($\text{HgNH}_2\text{Cl} + \text{Hg}$).

The reaction of mercuric ions with hydrogen sulphide forms a black precipitate, mercuric sulphide, HgS , insoluble in nitric acid but soluble in aqua regia:

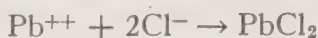


Mercuric chloride reacts with stannous chloride to form mercurous chloride (white) or mercury (gray):

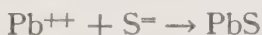


This test is used for mercuric ions with stannous chloride as the reagent or for stannous ion with mercuric chloride as the reagent.

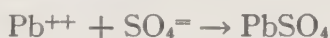
Lead Ion. — The reaction of lead ions with chloride ions forms a white precipitate of lead chloride, PbCl_2 , soluble in hot water:



With hydrogen sulphide, lead ions form a black precipitate of lead sulphide, PbS , soluble in nitric acid:



When lead ions react with sulphate ions, a white precipitate of lead sulphate, PbSO_4 , is formed:



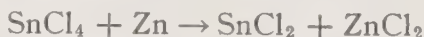
Stannous and Stannic Ions. — The reaction of stannous salts with hydrogen sulphide forms stannous sulphide, a brown precipitate soluble in hydrochloric acid (concentrated):



Stannic salts react with hydrogen sulphide to form stannic sulphide, a yellow precipitate soluble in hydrochloric acid (concentrated):



Stannic chloride may be reduced to the stannous salt with a reducing agent such as the metal tin or zinc:

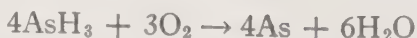


A solution of stannous chloride reacts with mercuric chloride to form HgCl , white or Hg , gray (see test for mercuric ion).

Arsenious Ion. — The reaction of arsenious salts with hydrogen sulphide forms arsenious sulphide, As_2S_3 , a yellow precipitate insoluble in dilute acids.



In the Marsh test (Chapter XXIII), the burning of arsine gas, AsH_3 , in limited oxygen forms a black deposit of arsenic as the flame strikes a cold surface:



CHAPTER XXVIII

RADIUM AND RADIOACTIVITY

RESEARCHES in the chemistry of radioactive elements are among the most outstanding and important of recent years. These researches began when Madame and Monsieur Curie discovered the presence of two radioactive elements, polonium and radium. After their discovery Madame Curie continued to study these elements. Her contributions to the studies of radioactivity and of the properties of disintegration of these elements have led to unprecedented advances in chemistry, in physics, and in medicine. From the study of the property of disintegration, chemists have discovered other radioactive elements and have gained an insight into the structure of all atoms. This same study has led physicists to devise theories about the nature of electricity. Physicians have used the rays emitted from radium in the treatment of diseases of a cancerous nature. A closer relationship between chemistry and physics has developed through the preparation of electrical rays similar to radioactive rays. Studies are in progress to determine the effectiveness of these electrical rays in medicine.

The name of Madame Curie is familiar to every person interested in science. She and her daughter, Irene Joliot-Curie, are the only women to have been awarded the Nobel prize in science. Madame Curie was awarded the Nobel prize twice, once in Physics and once in Chemistry, an honor which no other scientist, man or woman, has yet achieved. The story of her life, her untiring efforts in the search for radium and the study of its properties, and her interest in all advances made by other scientists in this study is most interesting.

Madame Curie, whose maiden name was Marie Sklodowska, was a native of Poland. Her parents were teachers in the city of Warsaw. At the age of fifteen she was graduated with first rank from the high school in Warsaw and became a governess in a Polish home. Because the Russian government in Poland strongly opposed any advancement by the Polish people, there was no opportunity for Marie Sklodowska to undertake further school work. For several years she could study only by herself,

sometimes attending secret meetings where young people discussed various subjects of interest. When she was twenty-four years old her ambition to study in Paris was fulfilled, and she entered the physical science course at the Sorbonne.

During her first years in Paris Marie Sklodowska lived in a little garret room and prepared her own meals. It is said that she carried coal to this sixth-floor room to use in the little stove which heated her home. In spite of many privations, she tells us that her life here was one of complete satisfaction because she was free to study and work undisturbed. After four years of study she married Pierre Curie, a professor in the school of physics and chemistry in Paris. Both were intensely interested in research, and they worked together in the laboratory on various problems in the field of physics.

When the studies of Madame Curie indicated the existence of a new element the two scientists worked together unceasingly on the problem, one of the most difficult pieces of scientific research of the century. They had only a poor laboratory, an abandoned machine-shop, in which to work. Tons of earthy material were extracted with acid, and the solution concentrated and analyzed, before it was definitely shown that the two elements were present. Seven tons of pitchblende contain only one gram of radium. It is a difficult task today to separate radium from its ore by the analytical methods that have been developed; it was many times more difficult when nothing was known of the properties of radium.

In 1903, the Nobel prize in physics was awarded jointly to the Curies and Becquerel for their important discoveries. In 1906, just as their work was being recognized in France and a new laboratory was being made available for them, Monsieur Curie was killed in an accident. Madame Curie was offered the position which her husband held at the time of his death, that of assistant professor of physics at the Sorbonne, a rank that no other woman had ever held. In 1911 she was again awarded the Nobel prize, this time in chemistry because of her extensive work on polonium and radium.

Madame Curie was especially interested in the therapeutic use of radium and studied extensively the physiological effects of the element. During the World War she was actively engaged in hospitals near the front teaching the use of radiological apparatus and when necessary using it herself for the alleviation of suffering. Soon after the war the women of America united to raise \$100,000 to buy one gram of radium to give to Madame Curie. Later another gram of radium was given to her by Americans interested in the control of cancer. These contributions, as well as the researches carried out by Madame Curie, were credited to the universities with which she had been associated. In 1934 this remarkable woman, having enriched the entire world with new tools of research and medicine, died from infirmities caused partly by her continued contact with the radioactive element.

The Curies had two daughters. Irene Joliot-Curie is a scientist as well known as her mother, and with her husband a winner of the Nobel prize in science. Eve Curie is a noted musician and the author of the interesting story of her mother's life.

Uranium, the First Radioactive Element. — In 1896, Henri Becquerel, a French physicist, made the discovery that when photographic plates wrapped in black paper were placed near minerals that contained uranium they were affected as if they had been exposed to light. After further study he found that uranium emitted invisible light rays of such short wave-length that they could penetrate black paper. He observed also that the electroscope, an instrument used to detect the presence of ions in the air, was affected by being placed near uranium. Madame Curie at this time was seeking for a problem to use as the subject for the research for her doctorate in science. She became interested in the discoveries of Becquerel and decided to investigate them further.

Pierre Curie designed a sensitive electrometer to measure the intensity of the radiations indicated by the electroscope. With the aid of this instrument the Curies were able to prove that the intensity of the radiations from any mixture was proportional to the concentration of uranium. It was independent of the temperature and of the other elements present. They gave to this property of emitting rays the name of radioactivity. Practically all other known elements were examined for this property, and only thorium was found to give out similar rays.

Clue to New Elements. — The study of uranium ores gave Madame Curie a clue to the presence of undiscovered elements. A few minerals, which contained only small amounts of the two elements that were known to be radioactive, were shown by the electrometer to have a more intense radioactivity than pure uranium. One of these, pitchblende, had an intensity four times that of uranium. It was evident that some unknown element must be present in these ores. Chemical analyses of pitchblende accounted for over 99 per cent of its composition. This meant that pitchblende contained less than 1 per cent of the new element. Hence it fol-

lowed that the radioactivity of the new element must be more than 100 times that of uranium, because an ore that contained less than 1 per cent of the element was more active than uranium. A search for an unknown element with 100 times the radioactive power of uranium was thrilling, but the results the Curies obtained were more exciting than they had anticipated. Instead of one new element, two were identified. These were present in a concentration of less than one-millionth, meaning that their activity is more than one million times that of uranium. The radioactivity of radium is so intense that in high concentrations it glows in the dark. It destroys cancer cells and bacteria and causes sores on any part of a healthy body that may come in contact with its light.

Discovery of the New Elements. — In searching for the unknown elements in pitchblende the Curies employed analytical methods similar to those we have studied in our laboratory work. At each step they tested with the electrometer the radioactivity of the precipitates and the filtrates, to determine where the radioactive elements were being concentrated. The mineral was dissolved in acid, and from this solution the insoluble sulphides were precipitated with hydrogen sulphide. Although uranium and thorium remained in the filtrate, the precipitate showed a decided radioactivity. When the precipitate was heated in a vacuum, the sublimate had an activity that was 400 times that of uranium. The new element thus demonstrated was given the name **polonium**, in honor of Madame Curie's native country.

In further analyses the fraction containing barium was found to have an intense radioactivity. When the barium was precipitated with sulphuric acid, the radioactive substance was precipitated with it. The radioactive element was finally separated from barium by the formation of a chloride, the solubility of which was different from that of barium chloride. The concentrated substance, one million times as radioactive as uranium and spontaneously luminous, was given the name **radium**. Because radium is similar to barium, it was placed below barium in Group II of the periodic table. In 1902 Madame Curie obtained enough

pure radium chloride to determine its properties. From 0.1 g. of the salt which she had separated she was able to determine the atomic weight of radium as approximately 225, thus definitely proving it to be a new element.

Disintegration of Elements. — Experiments with the radioactive elements have shown that the rays emitted are of three distinct types. These are designated as **alpha**, **beta**, and **gamma rays**. The alpha rays or particles have been shown to be nuclei of helium atoms with an excess of two positive charges. These obtain electrons and change to helium gas soon after they are emitted. They are unable to pass through a sheet of thin paper. The beta rays have been shown to be electrons (negative electrical charges). They travel with a speed almost as great as that of light, will pass through paper but not through a thin sheet of metal, and are deflected easily by a magnetic field. The gamma rays are light rays with a wave-length slightly shorter than that of X-rays. They can pass through thick sheets of lead. These rays represent the energy evolved by the atoms in disintegration.

Besides these three types of rays, a radioactive gas is always found among the disintegration products of radium. This gas has properties similar to those of the inert gases and has an atomic weight slightly less than that of radium. Hence it has been placed under xenon in Group 0 of the periodic table with the name **radon**. Hospitals use it in place of radium, calling it radium emanation.

Physiological Action of Radioactive Elements. — The short X-rays emitted by radium, radon, and other radioactive elements are injurious to living tissue. Early workers developed skin sores from handling concentrated preparations of radium. Further investigation demonstrated that, while the rays are destructive to all living tissue, cells which are actually in the process of dividing and growing rapidly are especially sensitive to them. Cancer and ringworm cells are dangerous because they grow and multiply so much more rapidly than other tissue, but this same property makes them especially sensitive to the gamma rays of radium. When growths of this type are exposed to the gamma rays, or to

the less expensive X-rays, the diseased cells are destroyed while the body cells are only slightly injured. Radium and radon have an advantage in this treatment because tiny tubes containing them may be inserted in places where they can affect only the diseased cells without exposing much of the surrounding tissue to their action.

Whenever radium is absorbed, or taken with the food, or used in radioactive waters, it accumulates with the calcium in the bones. No method has been found to successfully remove it from the body. Here in the bones the three types of rays continue to be emitted, disintegrating the bones and eventually causing death.

Transmutation by Radioactivity. — The disintegration of radium into two elements, radon and helium, made necessary a revision of the ideas of the element held by scientists. The modern theories of atomic structure indicate that the elements of high atomic weight have nuclei with such an unwieldy structure that they are easily broken down. We know that radium is not a compound of helium and radon, for it fits into the periodic table and acts chemically like other members of the group. Moreover no process has been observed by which the rate of disintegration can be accelerated or slowed down.

A knowledge of the mechanism by which the radioactive elements are disintegrated and new elements formed (a process called transmutation) has aided in the understanding of the structure of atoms. Whenever an alpha particle (which is a helium nucleus consisting of two neutrons and two protons) is emitted from the nucleus of an atom of radium, the atomic weight is automatically reduced by four. At the same time two electrons leave the planetary system, without any change in energy, to keep the atom neutral. This reduces the atomic number by two. If we follow these changes on the periodic table, we find that the element radon corresponds to this description; that is, the atomic weight of radon is 222 (radium, 225.97) and the atomic number is 86 (radium, 88).

Some of the radium atoms, instead of emitting alpha particles, give up beta rays or electrons that appear to come from the nu-

cleus. Since the electron has no appreciable weight, there is no change in atomic weight but after a rearrangement of the electrons a new element is formed with an atomic number one greater than the original. Scientists have calculated that because of these two types of disintegration radium will lose one half of its intensity in 1,690 years, or it is said to have a half-life of 1,690 years.

All elements with an atomic weight of 210 or greater are radioactive, some emitting only alpha particles, and others only beta rays, while some, like radium, emit both. Potassium and rubidium also show a weak emission of beta rays. These transmutations make possible many isotopes with atomic numbers between 82 and 92, although some of these are so short-lived that they are of little importance. One isotope of polonium has a half-life of only 10^{-6} seconds. Uranium has a half-life of 10^9 years and thorium of 10^{10} years. The gamma rays from these elements are produced too slowly to be of value. Only radon and mesothorium, an isotope of radium, are found in sufficient amounts and with the proper half-life to be used in place of radium. Radon has a half-life of 3.85 days and must be used quickly. Mesothorium has a half-life of 6.7 years.

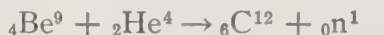
To distinguish between the isotopes formed by this transmutation they may be written with their atomic number as a subscript at the left and the atomic weight as a superscript at the right. Thus ${}_{88}\text{Ra}^{226}$; ${}_{88}\text{MsTh}^{228}$; and ${}_{84}\text{Ra-A}^{218}$ represent radium with an atomic weight of 226 and atomic number 88, mesothorium with an atomic weight of 228 and atomic number 88, and radium-A (a disintegration product of radon) with an atomic weight of 218 and atomic number of 84.

Artificial Transmutation. — In 1919 Lord Rutherford of England, by exposing nitrogen to the bombardment of alpha particles, was able to demonstrate that hydrogen and an isotope of oxygen could be formed from nitrogen. This change may be written using the complete symbols:



Following this, similar bombardment caused many of the lighter elements to be changed to heavier elements; magnesium, for example, may be changed into hydrogen and an isotope of aluminium.

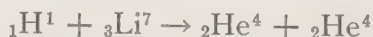
About 1930, the existence of neutrons was discovered when atoms of beryllium were bombarded with alpha particles. This transmutation may be written:



These neutrons proved to be of greater efficiency than the alpha particles in causing transmutation because without an electric charge they could penetrate into the nucleus more easily.

More recently a new unit, the **positron**, with a positive charge but with the same negligible weight as the electron, has been discovered when certain atoms were bombarded by X-rays. Positrons soon collide with an electron and thus become neutralized; so are of little practical value.

In 1932 two Cambridge chemists (Cockroft and Walton) used an electrostatic generator to impart energy to protons. These high speed-protons, when projected against lithium, caused some of the lithium atoms to change to atoms of helium.



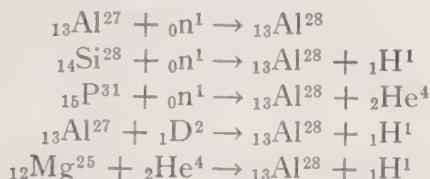
Thus these chemists were able to cause transmutation without the aid of alpha particles from radioactive elements.

Many other means have been used to disintegrate elements and bring about transmutations. They include electrons, either from radioactive elements or from X-ray tubes; protons made from hydrogen gas "ionized" by powerful X-ray tubes; deuterons, or ionized heavy hydrogen; and cosmic rays.

Artificial Radioactivity. — Early in 1934, Monsieur and Madame Joliot-Curie, son-in-law and daughter of Madame Curie, observed that when they bombarded boron, aluminium, or magnesium atoms with alpha particles the emission of positrons (and in the case of magnesium also electrons) continued after the alpha particles were removed. Thus they had obtained an artificial radio-

activity. Since then at least fifty elements have been made radioactive for short periods of time. The most interesting of these is the radioactive sodium in sodium chloride. This radioactivity has a half-life of 15 hours. It is hoped that this radioactive salt will be found useful in controlling human disease since its radiation does not continue for years as the radiation of the radium compounds does.

The extent to which artificial transmutation has progressed is illustrated by the fact that a radioactive isotope of aluminium with an atomic weight of 28 has been formed by five different methods, as shown in the equations:



In each of these cases the radioactive aluminium disintegrates emitting an electron according to the equation:



In 1938 a group of physicists were surprised to find that when they bombarded uranium with neutrons, radioactive barium atoms were emitted with a tremendous amount of energy. Further experiments showed that by this method atoms of either uranium or thorium, the heaviest elements on the periodic table, could be split into a variety of atoms about half the atomic weight of the original elements; and that the new atoms were always emitted with this vast amount of energy.

This was the first experiment in which atoms were actually split; in all previous experiments only an alpha particle or an electron was separated from the nucleus. Moreover the atoms formed in this disintegration were radioactive, because they contained a larger proportion of neutrons to protons than they were able to keep. In some cases neutrons were emitted forming atoms of a lower atomic weight. In other atoms the neutrons split into protons and electrons, and electrons were emitted, forming new atoms with a higher atomic number.

These experiments have encouraged the hope of some scientists that the vast store of energy in the atom may some day be available, not only because the energy obtained from this "fission" is so great, but because neutrons, the unit used for the bombardment, are formed again during the radioactivity of the products. If these neutrons can be made to split more atoms the action might be made to propagate itself, just as the heat from a small fire can cause more fire to start. The power that might theoretically be obtained from such a chain reaction is beyond imagination.

Recently French scientists obtained such a chain reaction. The chief obstacle to its practical use is that the atoms which undergo this change are those of a rare isotope of uranium (${}_{92}\text{U}^{235}$) and only traces of this isotope are available.

Uses of Radioactive Elements. — The use of radioactive elements in the control of cancer and ringworm growths has been mentioned. Radium and its isotope mesothorium are used also to make the luminous paints on watches and other articles.

Elements rendered radioactive artificially are now being used to study the distribution of metallic ions in the body. In one such experiment a person drank a solution of sodium chloride containing some radioactive sodium ions. The radioactivity was detected in the person's hand within two minutes, and increased in intensity for three hours. This indicated the rate at which sodium ions taken in food or drink are distributed through the body. Radioactive phosphorus and other elements have been fed in various forms to man and to animals and the rate of deposition in the bones and other tissues has been detected by radioactivity with the electroscope.

QUESTIONS AND PROBLEMS

1. Name six radioactive elements. Which two elements were discovered by the Curies?
2. Where do the radioactive elements occur on the periodic table?
3. Outline the method used by the Curies in the separation of the two new elements from ore. How was the electroscope used?

4. Give the nature of each of the three kinds of rays emitted from radioactive elements. How does each type of ray affect the structure of the atoms from which it is derived?
5. What is radon? Give another name for it. Compare its atomic structure with that of radium. Compare the half-life of radium and radon.
6. How are radium and radon used in hospitals? Why is radium dangerous?
7. Give four units used to bombard atoms and disintegrate them. Which unit is most effective?
8. Give two examples of artificial radioactivity. What practical uses are being made of it?

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CHAPTER XXIX

CARBON COMPOUNDS

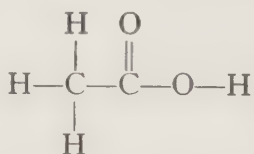
ORGANIC chemistry, sometimes called the Chemistry of Carbon Compounds, is one of the most important divisions of chemistry. The term organic has developed from the fact that most substances contained in, or formed from, living organisms are compounds containing carbon. Hence, the chemistry of carbon has come to be a study of the chemical changes associated with life processes.

At one time, compounds prepared in the laboratory were thought to be unrelated to those formed by life processes and were called inorganic. However, this distinction is not significant now, for chemists have learned to form in the laboratory many of the compounds associated with life processes. In fact, many similar compounds not known to be produced in nature, but which suit our needs better, are now produced by laboratory processes. Aspirin, sulfanilamide, and mercurochrome are closely related in structure to compounds produced by plants but are superior as drugs to any plant products. Chemists have learned to make the hundreds of coal-tar dyes by a study of plant and animal products, but those prepared in the laboratories are superior to any natural dyes.

A few carbon compounds were studied in Chapter XVI. Attention was then directed to the vast number of compounds of carbon which are present in living matter. A complete study of the 250,000 (or more) known compounds of carbon is obviously more than an entire course in the subject could include. This chapter is intended as an outline of the classes of compounds and as a short study of some of the simpler and more familiar of these compounds.

Types of Formulas. — The properties of organic compounds depend on the arrangement of the atoms in the molecule as much

as on the composition. For this reason carbon compounds are usually represented by graphic formulas, although they may be indicated by simpler types of formulas. The simplest type of formula, an **empirical formula**, indicates only the number of atoms of each kind in the molecule; for example, the formula we learned for sugar, $C_{12}H_{22}O_{11}$, and the formula for acetic acid, $C_2H_4O_2$, show only the composition of the molecules. A **structural formula** indicates the presence of certain groups and shows more fully the arrangement of atoms in the molecule. Acetic acid may be written as we have learned it, $HC_2H_3O_2$, or as we shall learn it, CH_3COOH . We have learned that the H at the beginning of a formula indicates an acid action. We shall learn that the group $-COOH$ is present in all organic acids and that the hydrogen of the $-COOH$ group is replaceable by a metal. A **graphic formula** must show by the valence bonds connecting the atoms the arrangement of the atoms and the valence of each atom. The graphic formula for acetic acid is



A number of organic compounds have the same empirical formula but have different structural and graphic formulas with a corresponding difference in properties. These compounds are called **isomers**. Since empirical formulas have so little significance we shall use structural and graphic formulas in our studies.

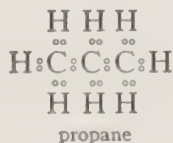
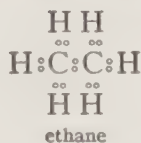
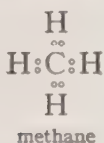
THE HYDROCARBONS

The periodic table indicates that the valence of carbon is four and that the formula for its hydride should be CH_4 . However the periodic table does not indicate that there are nearly 300 hydrides of carbon with different physical and chemical properties. These hydrides are known as **hydrocarbons**. They are of importance because they are the chief constituents of natural gas and petroleum and of the products obtained from petroleum.

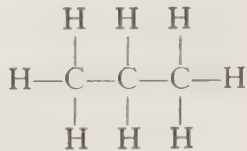
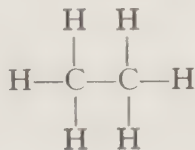
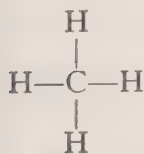
Some of the simplest of the hydrocarbons, with their empirical formulas, are:

CH_4	methane	C_5H_{12}	pentane
C_2H_6	ethane	C_6H_{14}	hexane
C_3H_8	propane	C_7H_{16}	heptane
C_4H_{10}	butane	C_8H_{18}	octane

The general formula for hydrocarbons of this type is $\text{C}_n\text{H}_{2n+2}$, in which "n" stands for any number of carbon atoms. They are **saturated hydrocarbons**, in which carbon links to carbon with one bond of valence, and the other bonds are attached to hydrogen atoms. In these formulas, the valence of carbon can be determined only by writing graphic formulas. It is a typical property of carbon to share electrons in covalent linkage and to form compounds which do not ionize. The covalent bond is shown in the following formulas in which hydrogen and carbon each furnish an electron of the shared pair (Chapter XII):



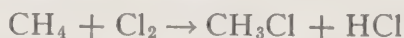
The formulas for ethane and propane show that carbon links to carbon in a covalent bond, a property which explains the great variety of carbon compounds. If these formulas are rewritten as graphic formulas, in which a single bond indicates the two shared electrons, they are simpler, and this method will be used in writing formulas for carbon compounds:



The saturated hydrocarbons vary in physical state as follows: the compounds containing one to four carbon atoms are gases, those containing five to sixteen carbon atoms are liquids, and those containing more than sixteen carbon atoms are solids.

Liquid petroleum is a mixture of many of these hydrocarbons, the gases and solids being dissolved in the liquid hydrocarbons. When petroleum is distilled, the mixtures of hydrocarbons are vaporized and may be collected in fractions having different boiling-points. The first fraction may be collected while the boiling-point of the distilling liquid is between 40° C. and 60° C. This distillate is called petroleum ether and is used as a solvent. While the temperature of the liquid rises from 60° C. to 70° C., the fraction that collects is gasoline. Other fractions contain the less volatile hydrocarbons with higher boiling-points, such as benzine and kerosene. In turn, fuel oils, lubricating oils, vaseline, and paraffin are obtained as products of the distillation of petroleum oil. The final residue is a solid tarry mass which has many commercial uses.

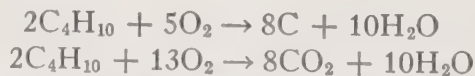
The saturated hydrocarbons react with chlorine or bromine by a **substitution reaction**, as follows:



By a long, slow treatment of methane with halogen other atoms of hydrogen are replaced by chlorine, forming in succession CH_2Cl_2 , CHCl_3 , and CCl_4 . Another typical reaction follows:

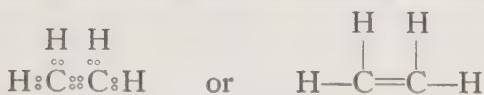


All hydrocarbons are readily combustible, a property utilized in the reaction which occurs when gasoline is burned in the cylinders of an automobile. When incomplete oxidation takes place, only the hydrogen is burned and carbon is deposited; complete oxidation of the hydrocarbon forms carbon dioxide and water. The following equations show the oxidation of butane to form carbon (incomplete oxidation), and to form carbon dioxide (complete oxidation):



The hydrocarbons just studied are known as saturated hydrocarbons to distinguish them from a group of compounds containing less hydrogen than the formula $\text{C}_n\text{H}_{2n+2}$ would indicate. In these compounds, known as **unsaturated hydrocarbons**, carbon

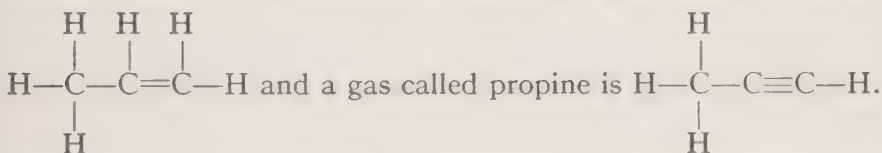
links to carbon with two or more bonds of valence, and the other bonds are attached to hydrogen atoms. The simplest of these, ethylene, has the empirical formula C_2H_4 . In this compound, carbon links to carbon by sharing two pairs of electrons (two bonds of valence) as shown in the following formulas:



In acetylene, C_2H_2 , carbon links to carbon by sharing three pairs of electrons (three bonds of valence) as shown in the formulas:

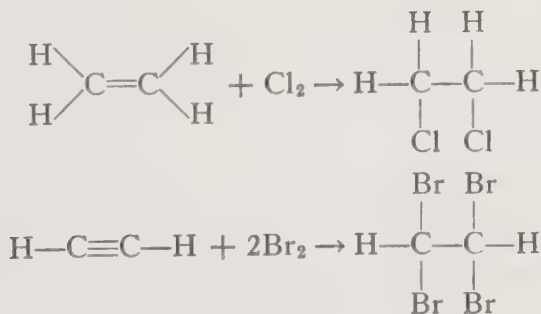


These compounds are called unsaturated because the extra bonds are easily broken, and the hydrocarbons have a tendency to combine with other active elements. Many similar compounds contain unsaturated groups; for example, a gas called propene is



The ending "ene" is used for the series of unsaturated hydrocarbons that have a double bond linkage ($-\text{C}=\text{C}-$) and the ending "ine" for the series of hydrocarbons having a triple bond linkage ($-\text{C}\equiv\text{C}-$).

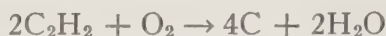
One of the most characteristic properties of unsaturated hydrocarbons is their ability to undergo **addition reactions**, such as the following:



The unsaturated hydrocarbons, like the saturated hydrocarbons, are readily combustible. Acetylene is used as a fuel gas. The complete oxidation of acetylene is represented by the equation:



Incomplete oxidation of acetylene may be shown as follows:



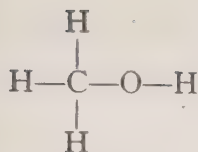
Derivatives of the Hydrocarbons. — *Halides.* These compounds have been mentioned as products formed by a substitution reaction in which the halogen takes the place of the hydrogen atoms in a hydrocarbon. The names and formulas for a few compounds are:

<i>Hydrocarbon</i>		<i>Halide</i>	
CH_4	methane	CH_3Cl	methyl chloride
C_2H_6	ethane	$\text{C}_2\text{H}_5\text{Cl}$	ethyl chloride
C_3H_8	propane	$\text{C}_3\text{H}_7\text{Cl}$	propyl chloride
C_4H_{10}	butane	$\text{C}_4\text{H}_9\text{Cl}$	butyl chloride

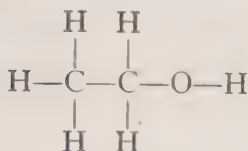
Thus, when one hydrogen atom of a hydrocarbon is replaced by halogen or some other element or group, a new series of radicals is formed; for example: CH_3 , methyl; C_2H_5 , ethyl; C_3H_7 , propyl; and C_4H_9 , butyl; as suggested by the foregoing formulas. These are known as **alkyl radicals** and will appear in many formulas in this chapter.

A few compounds in which more than one hydrogen of the hydrocarbon is replaced by halogen are: CHCl_3 , chloroform, an anæsthetic; CHI_3 , iodoform, an antiseptic; CCl_4 , carbon tetrachloride, which is a useful material for dry-cleaning and in certain types of fire-extinguishers; CCl_2F_2 , dichlorodifluoromethane (freon), used as the gas to be condensed in an electric refrigerator.

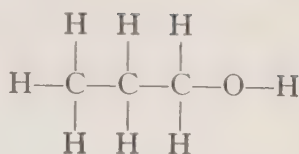
Alcohols. Alcohols correspond to hydrocarbons with the substitution of hydroxyl groups for one or more of the hydrogen atoms of the hydrocarbon. The graphic formulas and names for a few of the best-known alcohols are:



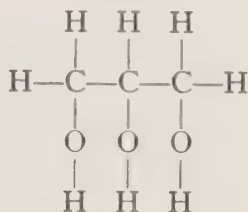
methanol
(wood alcohol)
(methyl alcohol)



ethanol
(grain alcohol)
(ethyl alcohol)

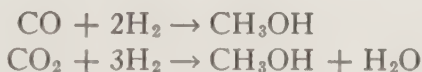


propanol

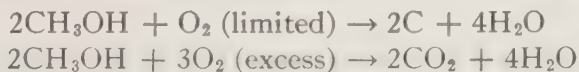


glycerol
(glycerin)

Methanol, the simplest of the alcohols, is also called wood alcohol and methyl alcohol. As suggested in Chapter XVI, it is obtained as a product of the destructive distillation of certain kinds of wood. It is also prepared synthetically by the reaction of carbon monoxide or carbon dioxide with hydrogen in the presence of a catalyst and under controlled temperature and pressure. The equations are:



Methanol burns with a hot flame and, like other carbon compounds, is oxidized to carbon in limited oxygen and to carbon dioxide in excess oxygen, as shown by the following equations:



Methanol finds use in industry as a solvent and in the manufacture of complex organic compounds. It is a poison and is often used in preparing denatured alcohol.

Ethanol is also called ethyl alcohol and grain alcohol. It is usually manufactured by the action of yeast on sugar solutions or a grain mash. The enzymes or catalytic agents present in yeast have the power of changing certain sugars into alcohol and carbon

dioxide. Although this is a complex process, the final reaction may be written as the equation:



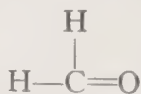
When grain mash is used, the starch present is changed to sugar by enzymes; this sugar in turn, is then fermented to alcohol by other enzymes.

The term alcohol, in commerce, refers to ethanol. It is this alcohol that is present in intoxicating beverages. Ethanol is used in the manufacture of complex organic compounds. It finds use as a fuel, as a solvent for perfumes, flavorings, and drugs; we buy vanilla and iodine in alcohol solution. Ethanol is used as an anti-freeze in automobile radiators, as a preservative, and as "rubbing alcohol" for hospital patients. At present, there is some interest in the production of alcohol for motor fuel.

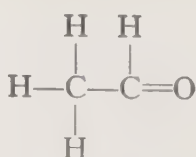
Commercial ethanol is usually denatured to render it unfit for a beverage, by the addition of a poisonous compound such as wood alcohol. Rubbing alcohol is denatured with substances that will not be harmful when applied externally.

There is a series of alcohols, similar to those just mentioned, but containing other alkyl radicals; for example, propanol, $\text{C}_3\text{H}_7\text{OH}$, and butanol, $\text{C}_4\text{H}_9\text{OH}$. These are less important commercially. Glycerol, $\text{C}_3\text{H}_5(\text{OH})_3$, better known as glycerin, can be considered as an alcohol derived from propane with three hydroxyl groups, each attached to a different carbon atom. It is a constituent of all fats. Glycol, $\text{C}_2\text{H}_4(\text{OH})_2$, is a synthetic alcohol used in anti-freeze mixtures.

Aldehydes. All aldehydes contain the group $\text{—}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}=\text{O}$ attached to hydrogen or an alkyl radical. The graphic formulas of the two simplest aldehydes are:

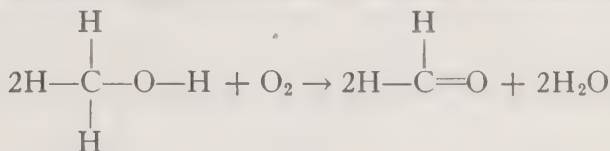


formaldehyde



acetaldehyde

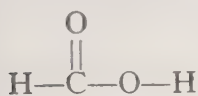
Aldehydes may also be considered as the first oxidation products of an alcohol. Methanol when oxidized forms formaldehyde.



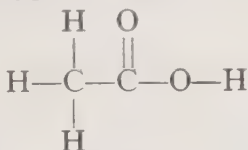
"Formalin," used as a disinfectant and as a preservative of zoölogical specimens, is a 40 per cent water solution of formaldehyde gas. Formaldehyde reacts with many compounds to make hard resin-like substances called **plastics**, which are used in the manufacture of buttons, fountain pens, combs, brush and mirror handles, jewelry, and many other articles. When formaldehyde reacts with phenol (a coal-tar product) the plastic formed is "bakelite." Other plastics are made by the reaction of formaldehyde with casein, with soybean protein, and with urea. (Urea, $\text{CO}(\text{NH}_2)_2$, can be made from carbon dioxide and ammonia.)

Acids. Organic acids are common in nature. They are responsible for the sour taste of many fruits and vegetables. The

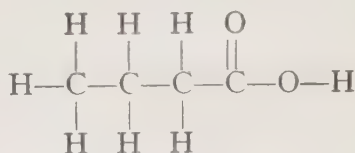
graphic formulas of organic acids contain the group $\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{O}-\text{H} \end{array}$, known as the **carboxyl group**. This may be noted in the following formulas of some typical acids.



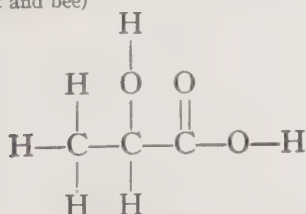
formic acid
(in the fluid from
certain organs of
the ant and bee)



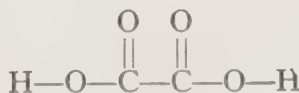
acetic acid
(in vinegar)



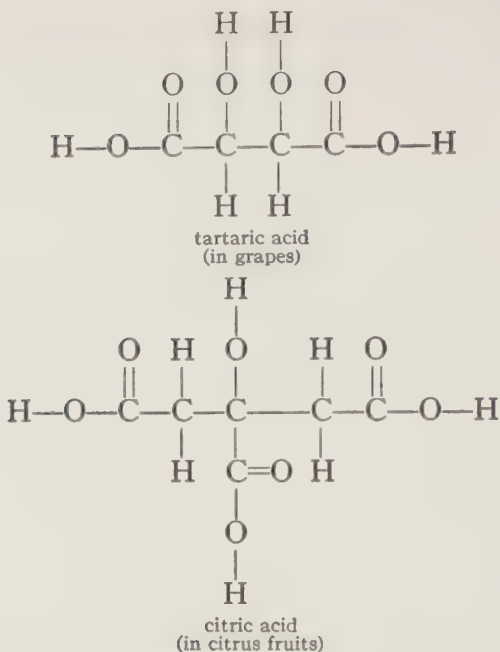
butyric acid
(in rancid butter)



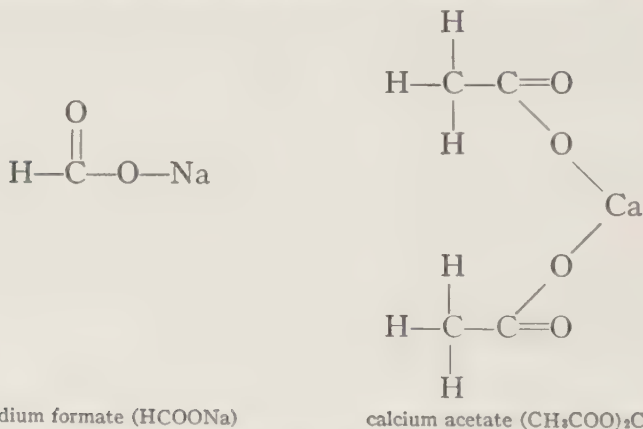
lactic acid
(in sour milk)



oxalic acid
(in leaves and stems
of some plants; a poison)

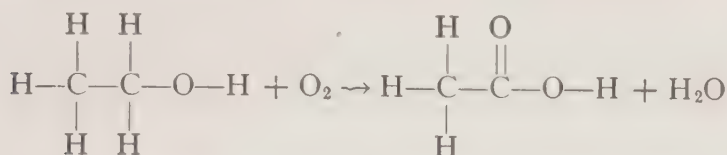


Organic acids are slightly ionized and are therefore weak acids. They form salts in which the hydrogen of the carboxyl group is the replaceable hydrogen, as shown by the formulas:



Commercial vinegar contains 4 per cent acetic acid. The manufacture of vinegar from fruit juices depends upon two chemical changes: (1) the fermentation of sugar to alcohol by yeast, followed by (2) the oxidation of alcohol to acetic acid by air or mi-

croörganisms in "mother of vinegar." The oxidation of alcohol is shown in the reaction:

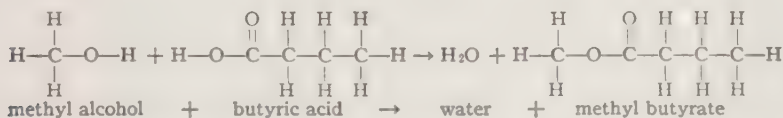


Organic acids that consist of an alkyl radical combined with one carboxyl group are called **fatty acids**, since many of them are constituents of naturally occurring fats. Acetic and butyric acids are among the simplest of these. Two typical fatty acids that are found in many fats are stearic acid, $\text{C}_{17}\text{H}_{35}\text{COOH}$, a white solid, and oleic acid, $\text{C}_{17}\text{H}_{33}\text{COOH}$, a liquid. Oleic acid is an unsaturated acid containing a grouping of the type $-\text{C}=\text{C}-$.



All unsaturated fatty acids and all low molecular weight fatty acids are liquids. Fatty acids that have a high molecular weight and have no unsaturated groups are solids.

Esters. The analogy between a salt and an ester may be shown by the definitions: a salt is a derivative of an acid in which one or more acid hydrogen atoms of the acid have been replaced by a metal; an ester is a derivative of an acid in which one or more acid hydrogen atoms of the acid have been replaced by a hydrocarbon radical. The formation of an ester is indicated by the following equation:



The esters have characteristic odors and flavors. They are formed during the growth of flowers and fruits and are responsible for many of the delicate fragrances of the flowers and the characteristic flavors of fruits. For centuries, man has engaged himself in making extracts from these natural sources and using them for perfumes and flavoring. The chemist has learned how to synthesize many of the same esters and can usually make them at less

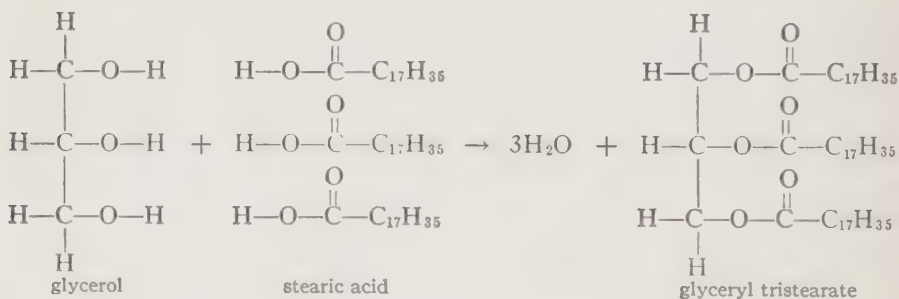
expense than by extraction from the flower or fruit. In this way, the chemist competes with nature in the preparation of compounds useful for perfumes and flavors.

The following tabulation gives a summary of formulas for some of the foregoing compounds and their relation to the hydrocarbons:

<i>Hydrocarbon</i>	<i>Halide</i>	<i>Alcohol</i>	<i>Aldehyde</i>	<i>Acid</i>	<i>Methyl Ester</i>
CH ₄	CH ₃ Cl	CH ₃ OH	HCHO	HCOOH	HCOOCH ₃
C ₂ H ₆	C ₂ H ₅ Cl	C ₂ H ₅ OH	CH ₃ CHO	CH ₃ COOH	CH ₃ COOCH ₃
C ₃ H ₈	C ₃ H ₇ Cl	C ₃ H ₇ OH	C ₂ H ₅ CHO	C ₂ H ₅ COOH	C ₂ H ₅ COOCH ₃
C ₄ H ₁₀	C ₄ H ₉ Cl	C ₄ H ₉ OH	C ₃ H ₇ CHO	C ₃ H ₇ COOH	C ₃ H ₇ COOCH ₃

FATS

A **fat** is an ester in which the alcohol radical is glycerol. The common fats of nature contain the acid radicals of butyric, C₃H₇COOH; oleic, C₁₇H₃₃COOH; stearic, C₁₇H₃₅COOH; palmitic, C₁₅H₃₁COOH; and other acids of high molecular weight. Although the fats of nature are not simple triglycerides, the following reaction illustrates the formation of a synthetic fat:

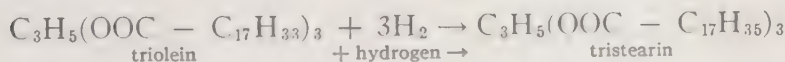


Glyceryl tristearate is also named **stearin** or **tristearin**. The names **palmitin** and **olein** are applied to the glyceryl esters of palmitic and oleic acids respectively. As to chemical composition, all fats are alike in containing the glyceryl radical but differ from each other in containing different organic acid radicals. It follows that the varying consistency of fats and oils must be associated with the chemical nature of the organic acids found in the fat molecules.

We have learned that fatty acids with a low molecular weight

or with unsaturated groups, $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ -\text{C}=\text{C}- \end{array}$, in the molecule tend to be liquid at room temperature. Similarly fats that contain radicals of liquid fatty acids in the molecule tend to be oils at room temperature. Thus, glyceryl oleate, containing unsaturated fatty acid radicals, and glyceryl butyrate, containing low molecular weight fatty acid radicals, are oils. On the other hand, glyceryl stearate, an ester of the saturated, high molecular weight fatty acid $\text{C}_{17}\text{H}_{35}\text{COOH}$, is a hard solid. The following natural fats contain successively larger percentages of olein (glyceryl oleate) and smaller percentages of stearin (glyceryl stearate); hence they increase in softness or liquidity — beef fat, lard, olive oil, cotton-seed oil.

Hydrogenation of Fats. — There is an increasing demand for edible solid fats, and there is also a surplus of vegetable oils such as peanut oil, cocoanut oil, and cotton-seed oil. All of the vegetable oils contain olein, having unsaturated acid radicals. As has been stated in the foregoing paragraphs, the unsaturated grouping readily undergoes addition reactions. Hence, when liquid fats are brought in contact with hydrogen in the presence of a catalytic agent, hydrogen atoms combine with the unsaturated molecules, forming saturated molecules which are solid fats. This change may be represented by the equation:

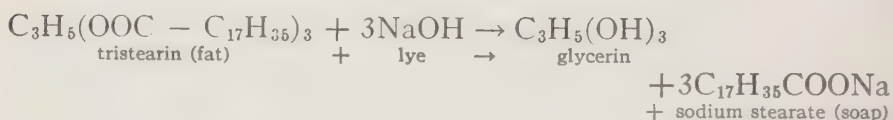


The reaction is called hydrogenation of fats. By this process vegetable oils are made into solid fats which are used in the manufacture of lard substitutes, oleomargarin, and soaps.

Soap. — Soap is a mixture of the sodium or potassium salts of certain fatty acids. Sodium oleate, sodium palmitate, sodium stearate, and the corresponding potassium salts are commonly used as constituents of soap. When a soap consists of potassium

salts, it is a soft or semi-solid soap; a solid soap consists of the sodium salts of the fatty acids.

The New England housewife made soap in her own home. The leaching from wood ashes furnished the alkaline solution; it consists of potassium carbonate and some potassium hydroxide. When the mixture of fat with this alkaline solution was boiled, a thick, semi-fluid potassium soap was formed. It was an impure soap, but effective in its cleaning properties. At the present time, when soaps are made in the home, lye, NaOH, is used instead of potassium carbonate as the alkaline solution. This makes a solid soap. Commercial soaps are made by using the same ingredients modified in a measure by the purpose for which the soap is to be used. The equation representing the reaction of tristearin with sodium hydroxide is as follows:



Soaps made from solid fats contain a large proportion of sodium stearate and are harder than soaps made from vegetable oils, which have a large proportion of sodium oleate (Chapter XXXIV). Some laundry soaps have naphtha or other solvents dissolved in them to aid in cleansing; scouring soaps may contain from 80 to 90 per cent of abrasive material.

Sodium and potassium are the only common metal ions that can be used in the preparation of soap, because of the fact that a soluble salt is necessary for a good soap. Such salts as calcium stearate, barium stearate, and magnesium stearate are insoluble in water.

CARBOHYDRATES

Carbohydrates are a group of compounds containing the elements carbon, hydrogen, and oxygen, the latter elements usually in the proportion found in water. Carbohydrates include sugars, starch, cellulose, gums, and similar substances.

Sugars. — Many different sugars are known as definite crystalline compounds. The names, empirical formulas, and sources of a few of the most important sugars are as follows:

Monosaccharides, those sugars which do not undergo hydrolysis:

Dextrose (glucose) $C_6H_{12}O_6$ fruits, honey
 Levulose (fruit-sugar) . . $C_6H_{12}O_6$ fruits, honey

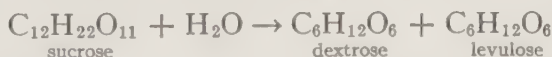
Disaccharides, those sugars which by hydrolysis are converted into monosaccharides:

Sucrose $C_{12}H_{22}O_{11}$ sugar-cane, sugar-beet
 Lactose $C_{12}H_{22}O_{11}$ milk
 Maltose $C_{12}H_{22}O_{11}$ prepared by action of malt with starch

Dextrose and levulose are isomers; that is, they have identical empirical formulas, but because they have a different arrangement of atoms in the molecule, there is a corresponding difference in the physical and chemical properties of the sugars. Sucrose, lactose, and maltose are also isomers.

Dextrose, often called corn sugar or glucose, is not as sweet and not as soluble in water as cane sugar; however dextrose is useful in the preparation of creamy candies and smooth ice creams. When dextrose is substituted for part of the sucrose in these foods, the dextrose delays crystallization and makes a soft smooth product. Levulose is sweeter, and more soluble in water than sucrose. Dextrose and levulose, as monosaccharides, are a ready-made source of energy for the body and are present in honey in about equal proportions.

Disaccharides, in the presence of acids or enzymes, undergo hydrolysis to form monosaccharides according to the reaction:



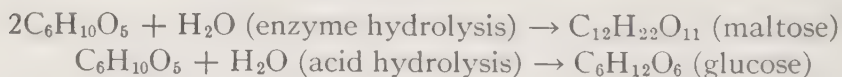
When hydrolysis of sucrose occurs, the process is called **inversion**, and the mixture of dextrose and levulose formed is known as **invert sugar**. Sugar-cane, sugar-beet, and maple sugar are the usual natural sources of sucrose. Crude sugars obtained by evapo-

ration of the extracts of cane or beet are purified to make the white crystalline product. The sucrose obtained is an almost pure chemical compound, whether prepared from cane or beets. Maple sugar is not purified because the impurities give the desirable flavor to the sugar.

Test for Sugars. Fehling's solution is a solution of cupric hydroxide in sodium potassium tartrate, $\text{NaKC}_4\text{H}_4\text{O}_6$. When heated with Fehling's solution, dextrose and levulose act as reducing agents upon the cupric ion (valence two) forming cuprous oxide, Cu_2O , a red precipitate. A solution of sucrose and of many other sugars will not reduce the cupric ion in Fehling's solution. When sucrose is boiled with hydrochloric acid until hydrolysis occurs, the product contains dextrose and levulose. This product will reduce Fehling's solution.

Starch and Dextrin. — From carbon dioxide and moisture, plants can build starch and store it in roots or seeds; such sources of starch are potato, corn, rice, and the cereal grains. Although starch from these various sources has the same chemical composition, an examination under the microscope reveals characteristic shapes and sizes for the starch granules from each material.

The formula for starch is written $(\text{C}_6\text{H}_{10}\text{O}_5)_x$, which indicates that the molecular weight of starch is not known, but that it is a multiple of the simple formula $\text{C}_6\text{H}_{10}\text{O}_5$. Hydrolysis of starch gives either the disaccharide or the monosaccharide, depending upon the catalytic agent used, as shown in the following equations:



Corn syrup is prepared by the hydrolysis of corn-starch with acid, forming a mixture of dextrin and dextrose. Corn syrup makes a soft smooth candy or cake frosting, because the dextrin helps to keep the sugar particles from becoming too large. When the sugar in corn syrup is crystallized, it forms the dextrose or corn sugar of commerce.

In the acid hydrolysis of corn-starch, most of the starch is

changed into dextrose, a sugar that forms a stable, supersaturated solution or syrup. Some of the starch is only partially hydrolyzed to dextrin $(C_6H_{10}O_5)_x$; in this formula, x represents a smaller number than in the starch formula. Dextrin is a viscous, gluey substance; in the corn syrup it keeps the glucose particles separated, preventing precipitation or sugaring. Dextrin is a valuable constituent of adhesive pastes. The glue of postage-stamps is a dextrin made from tapioca starch.

Under certain conditions, heat brings about the change of starch to dextrins. When bread is baked and when toast is made, the outside surface becomes brown; this is because some of the starch is exposed to intense heat and becomes dextrinized.

When starch is heated in water, the granules swell because they absorb water. The swelling causes the membranes that surround each granule to disintegrate. The starch is dispersed through the water to form a jelly-like mass. It is in this way that the cooking of starchy foods makes them digestible.

Test for Starch. Starch with iodine gives an intensely blue color; with dextrin, iodine gives colors varying from red to orange and finally yellow.

Cellulose. — Cellulose is the framework of all vegetable matter. The usual commercial sources are wood and cotton. Cellulose is fibrous in nature, is not disintegrated by boiling water, cannot be digested by the human digestive system, and gives no color with iodine. Cotton contains a high percentage of pure cellulose, while wood contains cellulose fibers bound together with lignin. When the wood is prepared for paper pulp, the lignin must be dissolved by calcium acid sulphite, $Ca(HSO_3)_2$, or some other chemical. This process leaves the wood cellulose as a mass of fibrous material which may be made into paper.

Cellulose molecules contain hydroxyl (alcohol) groups, which will unite with the hydrogen ion of an acid to form water and an ester; for example, cellulose nitrate. A completely nitrated cellulose is highly explosive, but a compound containing fewer nitrate groups is known as pyroxylin. Collodion is a solution of pyroxylin in a mixture of alcohol and ether. When used on a cut, the solvent

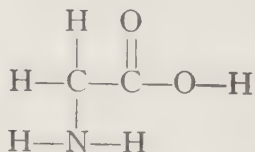
evaporates and the smooth, tough film of pyroxylin protects the wound. Finger-nail polish is a solution of pyroxylin and a dye in banana oil. Cellulose nitrate is the basic material for making smokeless gunpowders, celluloid, photographic films, lacquers, and patent leather. Because of its inflammability, pyroxylin is being replaced by cellulose acetate (another cellulose ester), and by the formaldehyde plastics.

PROTEINS

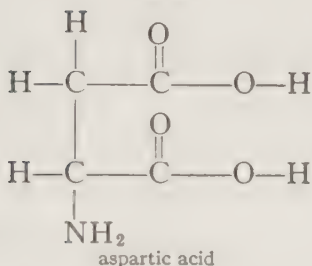
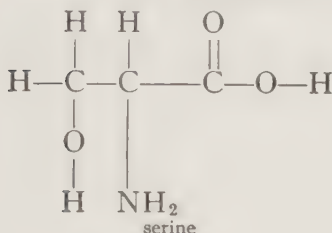
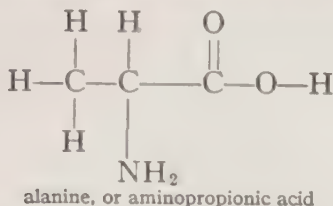
Proteins are present in all living cells and are essential to all life processes. They are complex compounds containing the elements carbon, hydrogen, oxygen, and nitrogen, and sometimes sulphur and phosphorus. Plants build their protein from the soluble compounds present in the air and soil; we build our protein from the plant and animal foods taken into the body. Some of the protein constituents of food are egg albumin, gelatin, casein in milk, zein in corn, and gliadin in wheat.

The protein molecule is very large; it may have a molecular weight of from 17,000 to 5,000,000. Each kind of protein tissue is built up so that the chemical composition is somewhat different. It is not so simple a matter to give a formula for proteins as for starch and fat. Attempts to determine the composition of proteins have been made through a study of the products of protein hydrolysis. Knowing the decomposition products of different proteins, chemists have been able to determine the kinds of matter that make up the protein molecules. These building materials are called **amino acids**.

The structure of an amino acid is shown by replacing one hydrogen atom of an organic acid by the **amino group** — NH_2 . Thus the graphic formula for glycine is



That is, glycine is aminoacetic acid. To show the variation in composition of amino acids, a few other examples are:

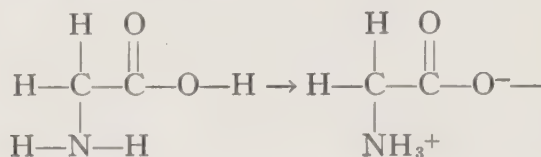


In natural proteins, there are known to be as many as twenty-five different amino acids. Tables are available giving the percentages of the different amino acids in gelatin, casein, gliadin, and other food proteins. In order to build body tissue, it is essential that our food contain a variety of these amino acids. Health and nutrition cannot be maintained on a food containing only one kind of protein, for all proteins lack one or more of the amino acids which are necessary for normal development. The nutrition expert will therefore need to be a chemist who knows the kind of amino acids in various foods and how to plan a diet containing an adequate supply of all the amino acids required for growth and maintenance of body tissues.

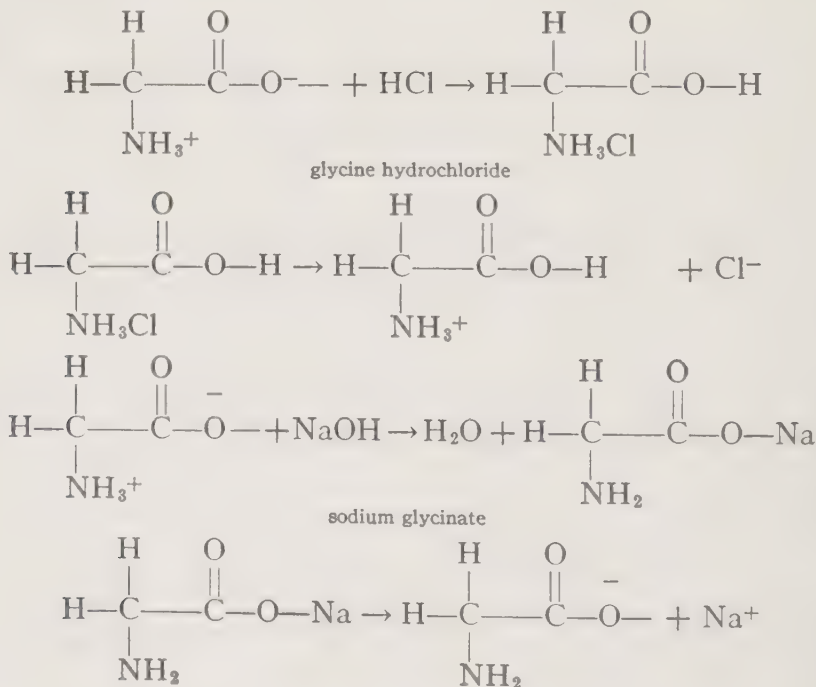
Amino acids are amphoteric in nature, since they contain both the basic amino group, NH_2 (which reacts much like NH_3) and

the acidic carboxyl group $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}-\text{H} \end{array}$ Unlike the amphoteric

compounds we have studied, the acid hydrogen of the carboxyl group reacts with the amino group forming an ion, one part of which is positively charged and one part of which is negatively charged. These are called **zwitterions**. Glycine, for example, forms the zwitterion as follows:



Like other amphoteric compounds, the zwitterions will react with either bases or acids to form salts which, in turn, ionize in an acid solution to give a positively charged amino acid ion and in basic solution to give a negatively charged ion as shown by the following equations:



The amphoteric reactions of amino acids are of interest because proteins, composed of many amino acids, have similar amphoteric properties. The amphoteric reactions of proteins will be referred to in the study of Colloids (Chapter XXXI) and of Textiles (Chapter XXXIV).

QUESTIONS AND PROBLEMS

1. Write the empirical and the graphic formula for a saturated hydrocarbon found in gasoline, one found in natural gas, and one found in vaseline.
2. How many grams of carbon will be formed from the incomplete oxidation of five liters of acetylene gas?
3. How many liters of oxygen will be required for the complete oxidation of eight liters of ethane gas?
4. How many liters of carbon dioxide will be formed from the oxidation of twenty grams of heptane? The volume of carbon dioxide obtained (at standard conditions) will fill how many liters at 20° C. and 730 mm. pressure?
5. Write the graphic formulas for ethylene and acetylene, showing the sharing of electrons in covalent linkage. Write the graphic formulas for ethylene and acetylene, using valence bonds. What is the valence of carbon in organic compounds?
6. Name six substances separated from petroleum by fractional distillation.
7. Write graphic formulas for the following:

(1) ethyl chloride	(6) sodium oxalate
(2) ethanol	(7) calcium formate
(3) acetic acid	(8) lactic acid
(4) sodium acetate	(9) glycerin
(5) oxalic acid	(10) ethyl acetate
8. Using graphic formulas, write equations to show the reaction of:
 - (1) a saturated hydrocarbon with halogen
 - (2) an unsaturated hydrocarbon with halogen
 - (3) methyl alcohol with acetic acid
 - (4) glycerol with formic acid
9. Write the graphic formulas for butane, butyl bromide, butyl alcohol, butyric acid, and ethyl butyrate.
10. Write the empirical formula for a saturated hydrocarbon with eight carbon atoms. Write formulas for a halide, an alcohol, an aldehyde, and an acid derived from this hydrocarbon.
11. Write equations for the incomplete and the complete oxidation of the following: ethanol, ethylene, acetylene, glycerol.

12. Write equations to show (1) the reaction of bromine with ethylene; (2) the reaction of chlorine with ethane; (3) four reactions of methane with chlorine.
13. What type of ester is a fat? Write an equation for the reaction of a fat with lye. What compounds are formed?
14. Use graphic formulas to write the following equations; name the esters formed:
 - (1) acetic acid with butyl alcohol
 - (2) formic acid with butyl alcohol
 - (3) butyric acid with glycerol
 - (4) lactic acid with ethanol
 - (5) butyric acid with ethanol
15. Use formulas and an explanation to show the difference in structure of a solid and a liquid fat.
16. How is a vegetable oil changed to a solid fat? What is the process called? Write an equation for the reaction.
17. Write an equation to show the hydrolysis of sugar. How does the reaction differ from that of the hydrolysis of salt?
18. Write equations to show the hydrolysis of starch by enzymes and by acid. Name the products formed.
19. Give a formula typical of each of the following classes of compounds; name each compound:

unsaturated hydrocarbon	carbohydrate
organic halide	aldehyde
alcohol	monosaccharide
fatty acid	disaccharide
ester	starch
fat	amino acid
soap	isomers
20. Explain the meaning of the term, zwitterion. Write an equation to show the reaction of glycine zwitterion with a base, and with an acid.
21. An experiment shows that 469 c.c. of acetylene gas at 10° C. and 780 mm. pressure weighs 0.58 gram. Does the gram-molecular weight of acetylene correspond to the formula CH or C_2H_2 ?
22. A volume of 450 c.c. of hydrogen gas at -15° C. and 750 mm. pressure is used to change triolein to tristearin. How many grams of triolein would be acted upon by this volume of hydrogen?
23. Ten liters of ethane gas, measured over water at 22° C. and 752 mm. pressure, enter into combination with sufficient oxygen to burn the ethane to carbon. How many grams of carbon are formed?
24. How many liters of chlorine gas at 18° C. and 750 mm. pressure will unite with 20 liters of ethylene (at standard conditions of temperature and pressure)?
25. At laboratory conditions, 18° C. and 745.5 mm. pressure, 875 c.c. of

methane gas was collected over water. The weight of methane was 0.5642 gram. Use the data to determine the weight of one liter of methane at standard conditions. What is the gram-molecular weight of methane?

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CHAPTER XXX

THE CHEMISTRY OF ARTIFICIAL HEAT AND LIGHT

EXCEPT for the recent application of electrical methods, the production of heat and light for our homes and factories is dependent almost entirely on the energy obtained by burning plant products. During the summer days, green plants receive energy from the sun which they transform to chemical energy in organic compounds, such as cellulose, starch, and sugar. Later this chemical energy is released by the process of combustion to give us heat on cold winter days or light on dark nights. Although we are primarily interested in the energy obtained rather than the changes in matter involved, a knowledge of these chemical changes is essential for a complete understanding of efficient methods for producing energy. Some of the simplest and most important fuels used in the home are wood, coal, peat, and lignite. These fuels have such similarity in composition and formation that they may well be studied together.

Wood and Charcoal. — Wood consists primarily of the organic compound cellulose $(C_6H_{10}O_5)_n$, which the plant prepares from the glucose manufactured in the green leaf. Mixed with the cellulose is water containing in solution various organic compounds such as sugar, turpentine, wood alcohol, and acetic acid, and several inorganic compounds of silicon, potassium, aluminium, and other elements. These inorganic salts have been absorbed with the water from the soil.

When wood is heated in the absence of air or in a limited supply of it, the organic compounds vaporize and the cellulose is decomposed into steam and carbon or charcoal. Commercial charcoal is made in this way. In earlier days, the wood was heated in out-of-door ovens and the organic compounds that vaporized were allowed to escape into the air or to burn at the entrance of the

oven. In modern ovens, however, these products are saved and form an important basis for the synthesis of more useful and complicated organic compounds in the laboratory.

When wood is burned in a stove or fireplace in which the supply of air is more or less limited, changes occur which are similar to those just mentioned. The organic compounds, burning as they escape from the wood, cause unburned carbon particles (or soot) to glow, thus forming yellow flames, while black charcoal is left on the grate. If a sufficient supply of oxygen is available, the charcoal also is burned, forming gaseous carbon dioxide and giving more heat energy. The ashes that are left are composed of the solid oxides of metals that were originally present in the wood in the form of various inorganic compounds. When fresh wood is added to a fire in a stove or fireplace, it is usually placed on top of the burning wood in the draft between it and the chimney. Thus, the wood is placed in an atmosphere of heated carbon dioxide containing a low supply of oxygen. The heat decomposes the wood and the glowing carbon particles that result form many-shaped and picturesque flames and then escape unburned into the chimney to settle as black smoke outside. If the fresh wood is placed under the burning wood, or to one side, there is less opportunity for luminous flames, but the more nearly complete combustion gives more heat with less black smoke.

Coal and Its Products. — Peat, lignite, bituminous or soft coal, and anthracite or hard coal are decomposition products of plant life. In past ages entire forests sometimes fell in shallow waters where, under the pressure of overlying vegetation and soil, the cellulose slowly decomposed into carbon and water while the other organic compounds gradually vaporized. In the places where these deposits have been subjected to the greatest pressure for the longest periods of time, anthracite coal, which is often 90 per cent carbon, is formed. In places where the pressure or the period of decomposition has been less, soft coal and lignite are found. Peat is formed from layers of grass or moss that have been slowly decomposing for a long period, probably since the

glacial age. It is being formed now in marshes throughout the world, where grasses and mosses flourish and then decay. Each summer the growth of past years is covered with a new layer. The approximate composition of these fuels is given in Table XXII.

TABLE XXII

APPROXIMATE PERCENTAGE COMPOSITION AND HEAT VALUE
OF SOME FUELS

<i>Fuel</i>	<i>Percentage of *</i>					<i>calories per gram</i>
	C	H	O	N	H ₂ O	
Anthracite coal	75-90	1	0.8	0.001	—	8,000
Bituminous coal	70-80	5	3-15	1.0	1-10	7,000-8,000
Coke	90-94	—	—	—	0.03-2	8,000
Lignite	35-60	5-7	4-25	1.50	6-15	6,000-7,000
Wood	44	5	38	0.06	11	3,000-5,000

* These fuels contain, also, varying percentages of ash.

Anthracite, soft coal, and lignite each burn differently and, as shown in Table XXII, they give up different amounts of energy. Anthracite coal is nearly pure carbon; that is, it contains a small proportion of the volatile carbon compounds. It burns slowly with a limited amount of flame and soot. Soft coal contains a larger percentage of carbon compounds and less free carbon. If it is burned in plenty of oxygen, the carbon compounds as well as the carbon of soft coal may be utilized. However, as it is often used, the carbon compounds are decomposed to form a tarry smoke which is not only a nuisance but a sign of wasted energy that might have been appropriated from the coal. Peat and lignite are so bulky that they are used as fuels only in communities near where they are found, and then only when other fuels are not available.

When soft coal is submitted to destructive distillation, three products are obtained: coke, an almost pure form of carbon; coal-tar, a black liquid containing several organic compounds; and coal-gas, which is a mixture of ammonia with methane, hydrogen, and other combustible gases. All of these products have important commercial uses. Coke, like charcoal and hard coal,

is a clean, slow-burning fuel. Coal-tar is a rich source of organic compounds such as benzene, naphthalene, toluene, and phenol. Such compounds are used as a basis for the manufacture of synthetic dyes, drugs, perfumes, and explosives. Coal-gas is washed by passing it through a dilute solution of sulphuric acid which absorbs the ammonia, forming ammonium sulphate. This is used as a fertilizer to add nitrogen to the soil. After washing and further purification, the gas is piped to homes and factories for heating or illuminating purposes. Since both coke and gas may be burned without the loss and inconvenience of smoke formation, and since the synthetic products made from the components of coal-tar are so valuable, destructive distillation is by far the most efficient method of using soft coal, and it will probably be practised more in the future.

Petroleum and Natural Gas. — In many localities certain forms of vegetation (or possibly animal life) have been submitted to pressure for long periods of time, forming the liquid called petroleum and a useful gas known as natural gas. The natural gas is usually found held under pressure in pockets above the petroleum. It is a mixture of low-molecular-weight hydrocarbons, and petroleum is a mixture of high-molecular-weight hydrocarbons. We have learned that by fractional distillation the petroleum is separated into naphtha, gasoline, kerosene, fuel oil, vaseline, and finally paraffin and other solid hydrocarbons. Fuel oil, slightly heavier than kerosene, is becoming popular as a fuel for heating the home, and kerosene is still commonly used as a fuel for cooking and lighting in rural communities. Paraffin candles are universal.

Parts of a Flame. — A candle represents a good, though old-time, device from which to study the parts of a flame. Candles consist of a central wick surrounded with paraffin, which is combustible. It is interesting to note that the center of a flame is not hot, so that the wick of a candle cannot burn away with the paraffin. The earlier type of candle had to have the wick snuffed or cut off every few minutes. Now the yarn used for a candle wick is always twisted, and thus bent in such a way that the end

is constantly burned away in the outside or hotter part of the flame.

Three distinct cones may be distinguished in a candle flame, a dark cone around the wick, a luminous cone about this, and another dark cone outside (Fig. 39). Below the flame, the paraffin is melted and held in the hollow at the top of the candle. The heat of the flame decomposes the carbon compounds present in the paraffin, forming combustible gases. Oxidation of these gases forms carbon dioxide and water and some unburned carbon in the form of smoke. The inside cone of the candle flame consists of hydrocarbons that have been melted by the flame, then drawn up through the wick by capillary action and vaporized. This zone contains only hot unburned gases. In the luminous zone incomplete combustion is taking place, forming particles of carbon heated to incandescence. A candle flame is used to give light, and hence this luminous zone is the most important part of the flame. In the outer cone of the candle flame complete combustion of the gases takes place; that is, this zone of complete oxidation is the hottest part of the flame.



FIG. 39. Candle Flame

Fuel Gases. — In connection with the study of other fuels, we pointed out the origin of the two most familiar fuel gases, coal-gas and natural gas. Where these are not easily available, manufactured gases have been devised to replace them.

Water-Gas. This gas is prepared by passing steam over heated carbon in the form of coal or coke. Under these conditions the

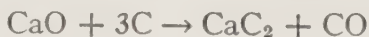
water is reduced and the carbon is partially oxidized. The equation follows:



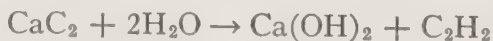
Both carbon monoxide and hydrogen are combustible gases suitable for fuels. The chief objection to this gas is that carbon monoxide is a powerful poison, and, as it has no odor, it may escape into a room without being detected.

Producer Gas. Certain industries find it profitable to burn coal in a limited supply of air to form the combustible gas carbon monoxide. The product, known as producer gas, contains the nitrogen of the air used in burning, and so has a low fuel value. Sometimes the gas is enriched by passing steam over the hot coke to form some water-gas. Producer gas is most efficient as a fuel gas when it is used as soon as it is prepared, and is still hot. It is an inexpensive fuel because a poor quality of coal or lignite may be used for its manufacture.

Acetylene. When lime and coke are mixed and heated in an electric furnace, the following reaction takes place:



The calcium carbide CaC_2 , a hard, gray, porous substance, reacts with water to form the unsaturated hydrocarbon acetylene as shown by the equation:



Acetylene gas has been used extensively in communities where other gases are not available. The solid carbide is easily and safely transported, and the preparation of the gas is a simple process. When this gas was used for lighting bicycles and the first automobiles, the solid carbide was carried in a container and the gas was generated as needed by dropping water on the carbide.

The approximate composition of some fuel gases is given in Table XXIII.

TABLE XXIII

APPROXIMATE PERCENTAGE COMPOSITION AND HEAT VALUE
OF FUEL GASES

<i>Type of gas</i>	<i>Percentage of *</i>						<i>calories per 1,000 liters</i>
	CO	CH ₄	C ₂ H ₄	C ₂ H ₂	H ₂	N ₂	
Coal-gas	9.0	34.0	—	6.6	47.0	2.3	6,300
Natural gas	—	83.5	12.5	—	—	3.8	10,000
Acetylene	—	—	—	100.0	—	—	14,000
Water-gas	45.8	2.0	—	—	45.7	2.0	3,800
Producer gas (enriched)	22.0	2.6	—	0.4	10.5	58.8	1,360

* Some of these gases contain, also, small percentages of carbon dioxide.

The Bunsen Burner. — Coal-gas contains such a large proportion of carbon that under ordinary conditions it burns with the yellow, luminous flame of incandescent carbon particles, and with the resulting heavy black smoke of unburned carbon. We owe to the German scientist Bunsen the development of a practical method for mixing sufficient air with gas to burn it completely, thus obtaining from it the maximum amount of heat. According to this method, some air is allowed to enter through holes at the base of the burner and mix with the gas. The size of the holes may be adjusted to give the proper combination of air and gas. All gas stoves and heaters, as well as the familiar Bunsen burner, are made on this principle.

The flame of the Bunsen burner consists of cones of different composition like those of a candle. The hottest part of the flame is in the outer cone, in which the actual burning is taking place. At the base of the flame where the gas enters, the temperature is low, a fact that may be demonstrated by placing a match-head held on a pin in the center of the base. The burner will be lighted several minutes before enough heat will be conducted through the metal of the pin to start the match-head burning.

The Welsbach Mantle. — Although the luminous flame of gas when burned is bright enough to be used for lighting homes, it is a wavering light, and the flame is smoky. To overcome this the Austrian chemist Welsbach devised the method of burning the

gas with a non-luminous flame inside of a mantle or bag composed of metallic oxides. This mantle, when heated by the burning gas, gives a steady, white light without smoke. More recently this mantle has been adapted for use with kerosene and gasoline lights.

Light without Heat. — Many chemists are disturbed because every method of producing artificial light depends on the process of heating a substance to incandescence. Even in electric lighting the filaments must be heated to incandescence before light is obtained. This means the production of a large amount of unwanted heat with a comparatively small return of light energy from the fuel used. The possibility of cold light is a problem of intense interest.

The neon light, described in Chapter XVIII, is one of the most efficient methods of transforming electrical energy into light. Recently, fluorescent lamps, based on the principle of the neon light, have been developed. For these lamps a glass tube is coated on the inside with certain compounds that fluoresce or give off light of a characteristic color when exposed to the invisible radiation of ultra-violet light. The glass tube is evacuated and small amounts of mercury and argon gas are introduced. The ends of the tube are fitted with electrodes and when an electric current is passed between them, the mercury vapor emits an ultra-violet radiation, which in turn causes the compounds coating the tube to glow. The argon gas assists in starting the action. It is possible to make fluorescent lamps that give a light closely resembling daylight.

A few elements, such as radium, are spontaneously luminous, but they are difficult to obtain; moreover, their decomposition cannot be controlled, thus making them impractical except for luminous dials of watches and similar purposes. Certain compounds, of which calcium sulphide is an example, are able to absorb light during the day and radiate it at night. Such compounds are now used to paint warnings along the highways. While the light may be seen for some distance on a dark night, it is not bright enough to light a room and becomes dim as the light absorbed is given up.

Fireflies, phosphorescent fungi in decaying vegetation, and a few kinds of bacteria and sea-organisms are capable of producing a true cold light. The luminous organs of fireflies contain two protein-like compounds: **luciferin**, which oxidizes and produces a cold light; and **luciferase**, an enzyme which catalyzes the oxidation of luciferin. When the firefly is dark, the oxidized luciferin is reduced to its original form ready to be used again. Although the chemist has not been able to duplicate the luminescence of the firefly, a number of compounds are known which, when oxidized, emit a cold light. Because the oxidized product cannot easily be reduced to use again, this method of producing light is still much too expensive to be practicable.

QUESTIONS AND PROBLEMS

1. Compare the origin and composition of wood, peat, soft coal, and hard coal. Explain the results obtained when each fuel is burned.
2. Compare the source of coke and charcoal. What are the by-products of each preparation? Compare the flames of these with the flames from other solid fuels.
3. What is a flame? Why does a wood flame differ from that of charcoal?
4. Diagram the parts of a candle flame; compare the composition of each part; compare the heat obtained from each part.
5. List some products of petroleum distillation.
6. Give sources and composition of five fuel gases.
7. Describe the action of a Bunsen burner, a gas stove, and a Welsbach burner.
8. Give two sources of "light without heat."
9. What are ashes?
10. Explain the action of the electric light.
11. Describe the construction of the fluorescent lamp. Explain the source of the light.

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CHAPTER XXXI

THE COLLOIDAL STATE

Introduction. — In the definition of a solution (Chapter III), it was stated that the solute is dispersed as molecules throughout the solvent. The molecular state of the solute makes it possible to consider that a solution is a homogeneous mixture. Suspensions of insoluble substances in water are not homogeneous and may usually be separated into a precipitate and a filtrate. Precipitates differ in the ease with which they may be filtered from the liquid containing them. Some consist of large particles which settle quickly and filter easily. Other precipitates, made of finer aggregates, settle slowly. A few precipitates cannot be separated by filtration from the liquid containing them because they are dispersed in particles that are smaller than the pores of any filter-paper. The individual particles are probably a large aggregate of molecules, but they are too fine to settle from the liquid or to be filtered from it. Such finely dispersed substances are said to be in the **colloidal state**.

In typical colloidal systems the dispersed particles are too small to be distinguished through a high-power microscope, although each particle is many times larger than an ordinary molecule. These systems are especially important because such substances have properties that are not common either to true solutions or to precipitates and because living matter is made up principally of substances in the colloidal state. Colloidal chemistry is a comparatively new study, and we will find that scientists often have only incomplete and unsatisfactory answers to many of the most fascinating and important questions concerning simple colloidal systems.

Colloids may be classified in a similar manner to solutions: that is, as solids, liquids, or gases dispersed in particles of colloidal dimensions through other solids, liquids, or gases. This

gives rise to a variety of systems, some of which have properties and appearances quite different from the finely divided precipitates just suggested. In all colloidal matter the substance that is dispersed in particles of colloidal dimensions is designated as the **dispersed part**, while the substance through which it is dispersed is called the **dispersion medium**. The dispersed part may be compared to the solute in a solution while the dispersion medium may be compared to the solvent. The individual particles of the dispersed part are spoken of as **micelles**, and the dispersion medium is called the **intermicellar liquid**.

A list of some familiar colloids will indicate their surprising abundance and importance in life.

- (1) Solids dispersed in solids
 - (a) Although most colored glass is made by dissolving colored salts in the molten glass, the best ruby glass has gold or selenium colloiddally dispersed in it to give the red color.
 - (b) Porcelain may be considered as a colloidal dispersion of opaque clay particles in a fused mixture of silicates or a glass.
 - (c) Many gems owe their color to colloiddally dispersed particles.
- (2) Liquids dispersed in solids
 - (a) Pearls consist of calcium carbonate (marble or limestone) with water colloiddally dispersed in it. The colors are caused by the reflection of light from the dispersed water.
 - (b) Opals consist of silicon dioxide (quartz) with water colloiddally dispersed in it. (Both pearls and opals are more lustrous when worn constantly or when kept in a moist atmosphere.)
 - (c) Cream cheese consists of casein from milk, with liquid butter-fat dispersed in it.
- (3) Gas dispersed in a solid
 - (a) White hair and white lilies owe their whiteness to air colloiddally dispersed in them.
 - (b) In cakes of fine texture, gas is finely dispersed throughout, giving them lightness.
 - (c) Coke and charcoal blocks always have gases or air colloiddally dispersed in them.
- (4) Solids dispersed in liquids
 - (a) Tea, coffee, and broth are not true solutions but contain colloidal particles as well as dissolved matter.
 - (b) In oil paints the pigment is colloiddally dispersed throughout the dispersion medium.

(5) Liquids dispersed in liquids

- (a) Milk consists primarily of liquid butter-fat and solid casein dispersed in water.
- (b) Gravy and white sauces consist of fat dispersed in water and held in droplets by hydrated starch particles.
- (c) The flesh of the body consists primarily of organic liquids colloiddally dispersed in other liquids in a rather unstable equilibrium.
- (d) Mayonnaise salad-dressing, while not a true colloid, consists of oil dispersed through vinegar in droplets, many of which are of larger than colloidal dimensions. These are stabilized by the constituents of the egg-yolk.

(6) Gases dispersed in liquids

- (a) Whipped cream, beaten eggs, and beaten gelatin are familiar examples.
- (b) Soda added to molasses gives a foam of carbon dioxide dispersed in a liquid.

(7) Solid dispersed in gas

Blue smoke and dust particles in the air are often colloidal. Black smoke and larger dust particles are small enough to have many of the properties of colloidal matter.

(8) Liquids dispersed in gas

Fogs and clouds consist of water particles condensed on dust particles dispersed in the air.

(9) Gas dispersed in gas

Since gases always form a homogeneous mixture with other gases, there are no colloids of this type.

Although the examples given do not all represent particles dispersed in true colloidal dispersions, they have properties that are typical of the colloidal state. In mayonnaise the droplets of oil may be as large as many precipitates, but there is a jelly-like consistency in the oil and egg-yolk mixture that is characteristic of colloidal matter. It is shown in the foregoing tabulation that there are many dispersion mediums. Of these water is the most familiar. It follows that the solid-in-liquid and the liquid-in-liquid types of colloid may be observed more often in our experiences.

Colloidal systems in which the dispersed part and the dispersion medium are mutually soluble are designated as **lyophilic** (medium-loving) colloids. Gelatin dispersed in water to form a

jelly-like solid or a viscous liquid is an example of this type because gelatin not only dissolves in the water but becomes hydrated as the water is absorbed. Colloidal systems in which the dispersed part and dispersion medium are not mutually soluble are said to be **lyophobic** (medium-hating) colloids. Tea, coffee, and oil paints are examples of this type. When water is the dispersion medium, the lyophobic colloids are designated as **hydrophobic** (water-hating) and the lyophilic colloids as **hydrophilic** (water-loving). Since water is the only important medium studied in this chapter, the latter terms will be used.

We have noticed that there is no sharp distinction between soluble and insoluble substances, but only a gradual change from the soluble to the insoluble substance or precipitate. Similarly, there is no sharp distinction between hydrophobic and hydrophilic colloids, but only a gradual change of properties. There is, however, a distinct difference between the typical hydrophobic and the typical hydrophilic colloid. Hydrophobic colloids usually form as liquids and resemble solutions. These are called **sols**. Typical hydrophilic colloids, on the other hand, are usually jelly-like solids and are called **gels**. Jelly and soap are typical gels, while custards, bread dough, and meat are more complex examples.

PREPARATION OF COLLOIDS

We are interested in methods for preparing colloids in the kitchen because soft, creamy foods are more palatable than tough or gritty foods. In the laboratory we prepare simple colloids in order to study their properties and to apply the principles learned when we have to deal with the more complex colloids met in various phases of life. Methods for the preparation of colloidal matter may be classified into two types. In one type we separate a substance in finely divided particles from a solution, and in the second type we disintegrate or disperse larger aggregates or precipitates into particles of colloidal dimensions. In either case the process must be controlled so that the particles formed will be of colloidal size.

Preparation of Colloids from Solutions. — When substances are precipitated from solution, the size of the particles varies with the conditions. If the precipitation takes place slowly, the first particles that separate serve as nuclei about which large crystals may grow. Such crystals are often found in thick sugar syrup or in honey that has been stored. If precipitation from a sugar syrup can be made to take place instantly, the nuclei form independently throughout the medium and have no opportunity for growth. In this way colloidal systems may be prepared. Three examples may illustrate the principle just stated.

1. *Preparation by Cooling a Liquid to Supersaturation.* When a substance is more soluble in hot water than in cold water, a supersaturated solution may be made (Chapter III). If the excess solute can be made to crystallize quickly, with the formation of many nuclei, it may form as a colloidal dispersion. This principle is of fundamental importance in making a soft, creamy fondant candy or fudge. A sugar syrup boiling at 113°C . (the soft-ball stage) is an unsaturated solution. It contains approximately 80 per cent of sugar. The solubility of sugar decreases rapidly as the solution cools. At 90°C ., the syrup containing 80 per cent of sugar is saturated and immediately becomes supersaturated as it cools below this temperature. In the supersaturated solution the addition of a crystal of sugar or slight agitation may cause the excess solute to separate in small nuclei. As the mixture cools, large sugar particles form by crystallization on these nuclei. If, however, all crystallization is delayed and the solution is allowed to cool until it is a highly supersaturated syrup, it becomes thick and viscous. Crystallization is then more difficult and it is necessary to beat the syrup to start precipitation. When it once begins, crystallization is almost instantaneous. As a result, many nuclei form throughout the solution and the product is a fine dispersion of sugar particles, or a soft, creamy candy.

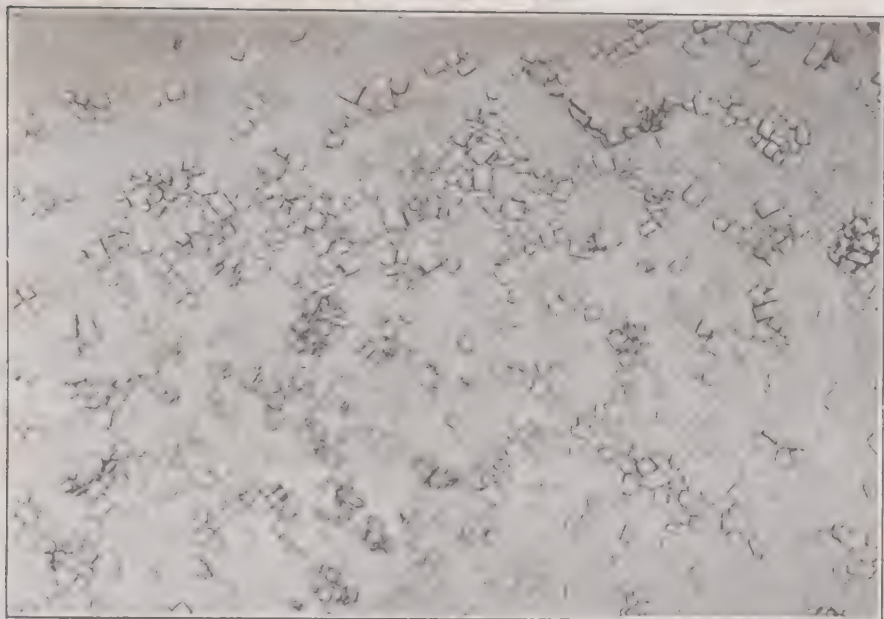
2. *Preparation by Chemical Reaction.* Many colloids may be made by double decomposition reactions; for example, the hydrolysis of ferric chloride may form ferric hydroxide in the colloidal state. The solution must be dilute, and the reaction must

be brought about in such a way that many nuclei form instantaneously throughout the solution. In this way there is no opportunity for the particles to combine in larger aggregates. Colloidal dispersions of barium sulphate and calcium oxalate may be formed during tests for these ions in dilute solutions. Instead of a heavy white precipitate, a milky liquid is formed that is neither a solution nor a precipitate, but is in the colloidal state.

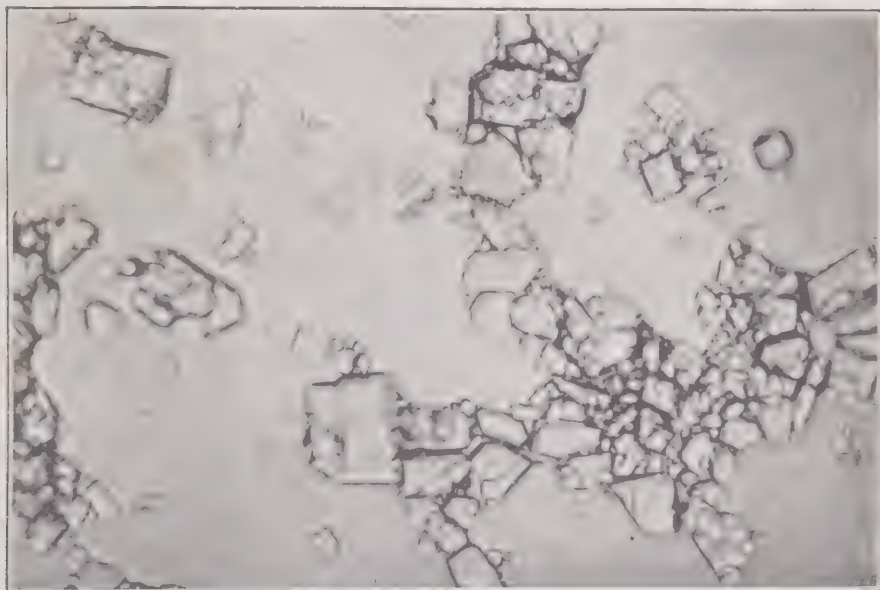
3. *Preparation by Replacement of Solvent.* If a concentrated solution of sulphur in alcohol is poured into water, in which sulphur is insoluble, the mixture becomes creamy white in color. As the alcohol mixes with the water, the sulphur molecules have no opportunity to become large aggregates, and so they form in particles of colloidal size. Another example of the formation of a colloid by replacement of solvent is found in the formation of white spots on a varnished surface. Many varnishes consist of resin in linseed oil. When water is dropped on such a varnish, it will become white and opaque from the colloidal dispersion of the resin particles in the water.

Preparation of Colloids from Large Particles. — When large particles are disintegrated into the dimensions of colloidal micelles, the process is called **peptization**. This can be accomplished by the following methods:

1. *Mechanical Dispersion.* It is possible sometimes to grind a substance to dimensions fine enough to give it colloidal properties. The clays used in making the finest china and cements settle slowly in water and are filtered from it with difficulty. When a precipitate consists of loose aggregates of colloidal particles, it may be dispersed in true colloidal dispersion by mechanical means. This is important in the dairy industry, for in the handling of milk the particles of butter-fat must sometimes be split into finer particles and emulsified into a homogeneous mass. The product is known as **homogenized milk** and is used in the preparation of evaporated milk and smooth ice-creams. In the manufacture of paints, the pigment is made into a homogeneous mass by dispersing it in a liquid by means of a colloid mill. In



a



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SUGAR CRYSTALS FROM FONDANT

These two pictures show the size of sugar crystals formed from a fondant sugar syrup (a) when the hot syrup (113° C.) was beaten immediately, and (b) when the syrup was cooled to 40° C. and then beaten.

making mayonnaise salad-dressing, an emulsion is formed by dispersing oil into droplets by mechanical means.

2. *Electrical Preparation.* When an electric arc is produced between gold, silver, or platinum wires immersed under water, the metal becomes colloiddally dispersed in the water (Fig. 40). The electric arc causes the metal to be vaporized and the vapor condenses into particles of colloidal size. It is interesting to note that the colloidal dispersion of gold formed in this way has the same ruby color as the red glass described in the list of colloids.

3. *Chemical Disintegration.* Certain reagents have the property of disintegrating solids into particles of colloidal size. In the

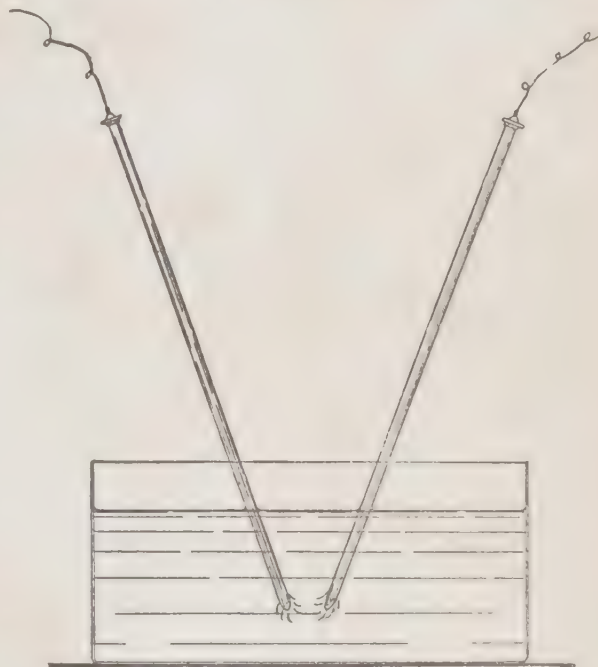


FIG. 40. Electrical Preparation of a Colloid

laboratory, heavy precipitates are sometimes disintegrated by the presence of an excess of one of the constituent ions. In this way, precipitates of silver chloride may become colloidal and impossible to filter if an excess of silver or of chloride ions is present in the liquid.

There are many examples of peptization by chemical reactions. Proteins and starches are disintegrated or peptized to form liquids by the action of the digestive juices. A little baking-soda added to dried beans or peas will hasten the disintegration of the tough fibers and make them soft and tender. When wool and silk textiles (proteins) are acted upon by sodium hydroxide, we have another

example of chemical disintegration of the fabric into a colloidal dispersion.

THE PROPERTIES OF COLLOIDS

The diameter of colloidal micelles is usually given as between 0.000001 mm. and 0.0001 mm. A dimension of this order can be more simply expressed in a unit smaller than the millimeter, namely, the micron (μ), which is a thousandth of a millimeter, or the millimicron ($m\mu$), which is a thousandth of a micron. Colloidal micelles measure between one and 100 millimicrons. Micelles which are much smaller lose their colloidal properties and act like solutions. As micelles become larger than these dimensions they may be distinguished under a high-power microscope, and their colloidal characteristics become less distinct. The limits are far from definite, and some properties typical of the colloidal state may be found in many suspensions, such as fine muddy particles in river water, as well as in some solutions of compounds with a high molecular weight, as sugar or proteins.

Optical Properties. — *Tyndall Effect.* When a bright light falls on finely divided material, such as a dust cloud in the air, each separate particle reflects the light which falls on it; as a result, a bright path of glowing light is formed. We have seen the sunlight shining through a tiny hole in the curtain in a dark room, causing a sunbeam or path of light due to reflection of the light by dust particles in the air. This phenomenon is known as the **Tyndall effect**, because a man named Tyndall first studied it thoroughly. The Tyndall effect is responsible for the colors of the sunset. The finely divided dust in the air reflects the light after the sun has fallen below the horizon. When the head-lights of an automobile form a path of light in a fog, we have another example of the same effect. The Tyndall effect is an important method of distinguishing solutions from colloidal sols.

A sol, such as tea or coffee or ferric hydroxide sol, appears to the eye as a clear solution. If such a sol is placed in a dark box and a beam of light from a pin-hole in the box shines through it, a path or cone of light, the Tyndall effect, may be observed. In the cone the larger particles may be observed sometimes as bright specks

of light. This effect is not obtained when a beam of light is passed through a solution.

Brownian Movement and the Ultramicroscope. In 1827 an English botanist, Robert Brown, while studying a suspension of pollen grains in water, noticed that the grains were in constant motion. In a further study of this phenomenon he found that when any finely ground material was suspended in water the particles were in constant motion. Later, it was demonstrated that this motion, now called **Brownian movement**, is caused by the bombardment of the particles by molecules of water.

Particles of colloidal dimensions cannot be distinguished under the microscope, and a hydrophobic colloid appears through the microscope the same as a clear solution. In 1904, a German chemist, Zsigmondy, devised a high-power microscope under which the Tyndall effect can be seen. A strong beam of light is passed through the sol, which is contained in a small black box on the stage of the microscope. Instead of the clear liquid that is seen through the ordinary microscope, one observes tiny, shapeless sparks of light. One of the best descriptions of the appearance of this phenomenon is that given by Zsigmondy of his first observation of a gold sol through the **ultramicroscope**. He said that the small gold particles appeared to float and move with astounding rapidity. A swarm of dancing gnats in a sunbeam gives an idea of the motion of the gold particles in the hydrosol of gold. They hop, dance, jump, dash together, and fly away from each other, so that it is difficult in the whirl to get one's bearings.

Electrical Properties. — Many of the properties of colloidal systems depend on the following factors: (a) the increase in surface area as the dispersed particles become disintegrated into colloidal micelles and (b) the development of an electric charge by each micelle. The increase in surface area may be illustrated by considering the surface exposed when a cube which measures one centimeter on each side is cut into particles of colloidal size. When uncut, such a cube has a surface area of six square centimeters and a volume of one cubic centimeter. If this cube should be cut in half in three directions, making eight cubes in all, each

measuring one-half centimeter on the edge, the total surface area of the one cubic centimeter of material would be increased to twelve square centimeters. If one should continue to cut this cube into smaller parts until each edge is 100 $m\mu$ or the dimensions of larger colloidal particles, it may be calculated that the total surface area of the one cubic centimeter of material would become 600,000 sq. cm.

The vast surface area of the micelles is especially important in giving colloidal matter characteristic properties because many factors act together to give the surface of each micelle an electric charge. In many cases the outside atoms on the surface of a micelle have a tendency to ionize, either losing or gaining electrons; as a result, the remaining part of the micelle has a net electric charge proportional to its surface area. In other cases the micelle attracts and holds electrically charged ions from the dispersion medium and thus obtains an electric charge. In a dispersion medium that is acid in reaction, with an excess of hydrogen ions, the micelles attract them and become positively charged. In a similar manner, the micelles attract the hydroxyl ions of a basic medium and become charged negatively. When a substance is disintegrated by mechanical action, as in a colloid mill, the micelles may become charged with electricity by a transfer of electrons — just as a hard rubber comb becomes electrically charged when used to comb the hair. These and other factors cause colloidal micelles to acquire an electric charge which, because of the increased surface area, may be immense.

An interesting experiment demonstrates that the micelles have electric charges. When a current of high voltage is forced through a sol, the micelles migrate slowly toward the electrode with the opposite charge. This migration is easily seen when the micelles are colored. Near one electrode, the sol is intensely colored, and it is faintly colored at the other electrode. Most natural hydrophobic micelles migrate to the positive electrode, showing that they are charged negatively. This is true of clay and mud particles suspended in water and of fog and smoke particles dispersed in air. Colloidal gold and platinum micelles are negatively charged. The ferric hydroxide sol has a positive charge. The

charge carried by dyes in solution depends on their chemical composition.

Precipitation. The charges on the surfaces of the micelles help to separate them and prevent the formation of a precipitate. Any condition that tends to remove the charges or neutralize them may cause a precipitate to form. This may occur when an electrolyte, or a sol containing micelles with the opposite charge, is added to any sol. The micelles, as they are neutralized, collect in large masses and settle in the medium or may be filtered from it like other precipitates. It is interesting to note that divalent ions usually have many times the efficiency of monovalent ions, and trivalent ions often have from 500 to 1,000 times the precipitating efficiency of monovalent ions. The principle of adding electrolytes to precipitate a colloid is used in city water systems when aluminium and iron salts are added to muddy water to clarify it for use in the home. The addition of trivalent ions accelerates the settling of the silt by neutralizing the charge of the micelles and causing them to collect in particles large enough to settle quickly.

Many hydrophobic colloids may be precipitated by the addition of a mere trace of electrolyte. The salts in tap-water are often sufficient to coagulate the micelles of some sols. Precipitation is hastened by boiling or agitating a sol. A few sols are so unstable that they will precipitate when heated or when shaken, without the addition of a neutralizing ion. Hydrophilic colloids, on the other hand, are stable and are not easily precipitated by neutralizing the electric charge. This stability may be explained by considering that each micelle of a hydrophilic colloid is surrounded by one or more layers of water. The only way to coagulate such hydrated particles is to remove the protecting layers of water molecules by some dehydrating agent. Alcohol, when added to hydrophilic colloids, will absorb the water and precipitate the colloid. This principle is applied in the kitchen when alcohol is added to fruit juice to test for the presence of pectin.

When large quantities of salt are added to hydrophilic colloids, the salt absorbs the water and then neutralizes the charge and precipitates the micelles. This process, known as **salting-out**, has long been used in the manufacture of soap. After the reaction of

the fat with lye in the soap kettle, large quantities of sodium chloride are added to the mixture. The water is withdrawn from the soap particles and precipitation occurs. The soap is lighter than the salt solution and rises to the surface, where it forms a solid gel that may be cut into cakes.

Protective Colloids. When hydrophilic colloids are added to hydrophobic sols, the layers of water that protect the hydrophilic micelles from being precipitated also exert a protective action on the hydrophobic micelles. When hydrophilic colloids are used in this way, they are designated as **protective colloids**. This property is quite familiar in cookery. Gelatin is perhaps the most common protective colloid. It is added to marshmallows to prevent the formation of large sugar crystals and to ice-cream mixtures to make a smooth, creamy product. Egg-white, another protective colloid, is used in making divinity candy, frostings, and ice-cream. The hydrated starch in white sauce acts as a protective colloid in custard ice-cream and in gravies. White sauce is used in making tomato soup because it tends to prevent curdling or precipitation of the milk.

Adsorption. — By the term **adsorption** is meant the concentration of a dissolved or dispersed substance at some surface. Adsorption occurs in the dyeing of textiles when the color leaves the dispersion medium and concentrates on the surface of the material until the textile has a much deeper color than the dye bath. The amount of substance that can be adsorbed from a solution or sol depends on two principal factors: (a) the intensity of the attraction of the surface for the dispersed substance and (b) the extent of area of the surface. Since in colloidal systems there may be a definite electrical attraction and the surface area is very large, it is evident that adsorption is an important factor in the study of colloidal matter.

We have noted (Chapter XXIX) that in acid solutions protein molecules become positively charged, and in basic solutions they become negatively charged. This fact has an important application in the dyeing of wool and silk textiles (protein material). Dyes are colloidal, and the micelles carry an electric charge, the

sign of which depends on the composition of the dye. Dyes with a positive charge will dye wool and silk in a basic solution, giving a fast color. They are known as basic dyes. Acid dyes have a negative charge. In an acid solution, the protein of the wool and silk is positive, and hence the acid dye is adsorbed and precipitated on the fabric. When salts of any type are added to the dye bath, the mutual precipitation or adsorption is aided by the precipitating action of the salts. On the other hand, dextrin, starch, and other protective colloids inhibit the adsorption of the dye.

We make use of the property of adsorption whenever we use blotting-paper to take up ink, or fuller's earth to remove a grease spot, or white of egg to settle coffee-grounds. Powdered charcoal is of importance as an adsorbing agent in industry. It is used to clarify colored solutions, especially the syrups prepared in refining cane and beet sugar. Charcoal is an adsorbent of gases and so is used in gas masks.

Diffusion. — One of the first properties that we observe in a study of colloids is the slow rate of diffusion through a membrane or gel, as compared with the rate with which substances diffuse when in solution. This is easily observed when we compare the rate of diffusion of a solution and of a colloidal sol through tubes of gelatin gel. The molecular dispersion diffuses through the gel

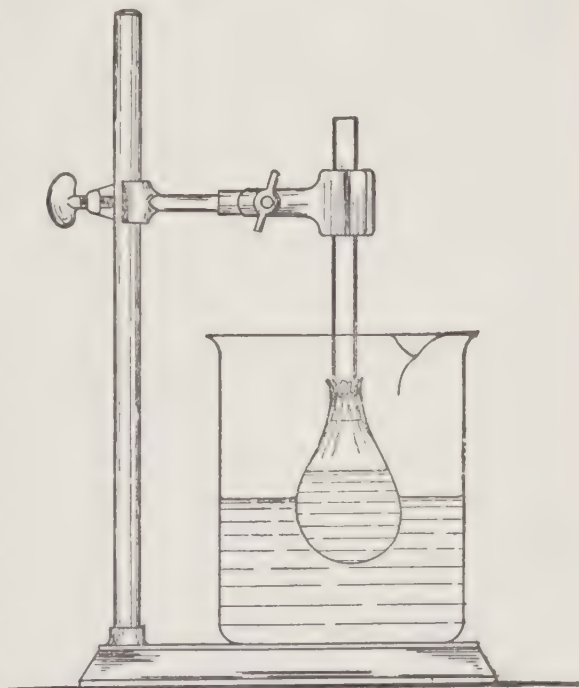


FIG. 41. Dialysis

rapidly, while the larger, slow-moving particles of the colloidal sols do not diffuse appreciably.

Dialysis. Membranes such as parchment paper and cellophane may be impermeable to colloidal micelles, but they may allow the passage of water and electrolytes. Membranes of this type are useful in the purification of colloidal systems. When hydrophobic sols are made by chemical reaction, they contain electrolytes in solution which have a tendency to precipitate the sols. To separate the electrolytes from the colloidal micelles, the impure sol is poured into a sac made of a membrane that will allow the electrolytes to diffuse through it (Fig. 41). This sac is placed so that distilled water flows around it for several hours. The electrolytes pass through the membrane and are washed away. The colloidal particles do not pass through the membrane and are retained in the liquid held by the sac. This process of separating the dispersed parts of a colloidal system from the soluble electrolytes by means of a membrane is called **dialysis**. The process of purification may be quickened by shaping the membrane in the form of a filter and using suction to draw the liquid through the membrane. This is called **ultrafiltration**. It is more rapid than dialysis but much slower than filtering a precipitate from a solution.

Properties Pertaining to Hydrophilic Colloids. — As was stated in the foregoing, there are characteristic differences between typical hydrophobic and typical hydrophilic colloids. The properties mentioned in the preceding paragraphs are, with certain reservations, characteristic of both types of colloids. Hydrophilic colloids have properties that are not shown by hydrophobic colloids. Moreover, we are especially concerned with them because gelatin, egg-white, meat, vegetable tissue, and some textiles are hydrophilic colloids.

Structure of a Gel. When a strip of dry gelatin is immersed in cold water, it absorbs the water and becomes softer and larger. The gelatin is disintegrated or peptized when hot water is added. The sol formed is viscous and consists of colloidal micelles of gelatin dispersed through the water. As the sol cools, it becomes

a jelly-like mass. When this occurs, the gelatin is in the form of colloidal particles with layers of water adsorbed on the micelles. Water is held between the micelles also. The mass is a solid gel of water dispersed in gelatin. Other hydrophilic gels have a similar structure, the dispersion medium becoming the dispersed part while the original dispersed part with the adsorbed layers of the medium (water) forms a solid structure.

Isoelectric Point. By the term **isoelectric point**, the chemist means that hydrogen ion concentration at which a colloid has no electric charge. It will be recalled that by adsorption many colloids acquire a positive charge in acid solution and a negative charge in basic solution. The isoelectric point is the hydrogen ion concentration midway between these two conditions. At this hydrogen ion concentration the micelles have no electric charge. As a result the properties of colloids at the isoelectric point are different from those at any other hydrogen ion concentration; for example, at this hydrogen ion concentration hydrophilic colloids are the least stable and the most easily precipitated. The isoelectric point of a colloid is not often at exact neutrality or a pH of 7. With proteins, it is usually at a concentration slightly more acid than neutral, often near a pH of 5, or at about the same pH at which methyl orange changes color.

Colloidal Properties of Proteins. — In Chapter XXIX we learned that protein molecules are large and may have molecular weights as high as 17,000 or even 5,000,000. Thus they are large enough to have colloidal properties even in solution. We learned also that proteins consist of a combination of amino acid molecules and react like them. Thus, they have amphoteric properties and exist as zwitterions similar to those of glycine. In acid solution, proteins form huge positively charged ions similar to the ion in glycine hydrochloride, and in basic solution they form huge negatively charged ions similar to the negative ion of sodium glycinate.

Since proteins exhibit the properties of colloids and at the same time act as chemical compounds, they may obtain an electric charge either by the colloidal adsorption of ions or as a result of

chemical action. Experiments indicate that both factors are involved and that in every case they obtain a positive charge in acid solution and a negative charge in basic solution. At the isoelectric point, near a pH of 5, the protein molecule has a minimum electric charge and is unstable.

In summary, we may consider that the charge upon the protein molecule may arise from a reaction or through adsorption. If it is caused by a reaction, it is through the formation of a compound such as sodium proteinate in an alkaline ($NaOH$) solution, or the formation of a compound such as protein chloride in an acid (HCl) solution. If the protein assumes a charge through adsorption, the charge is the same: that is, hydroxyl ions (negative) are adsorbed in an alkaline medium, and hydrogen ions (positive) in an acid medium.

Hydration. The adsorption of water by the micelles of colloids is known as **hydration** and is one of the most important properties of hydrophilic colloids. The sprouting of seeds depends on the hydration of the colloids under the right conditions. We note this same property when we soak dried beans or peas to soften them before they are cooked.

At the isoelectric point hydrophilic colloids are only slightly hydrated. Consequently, at this hydrogen ion concentration they are the most easily coagulated or precipitated. If either an acid or a base is added, hydration is increased and the hydrophilic colloids tend to swell and become more tender. This fact is painfully illustrated by a bee sting. The bee injects under the skin a tiny bit of an acid solution, causing the flesh to hydrate or swell. The swollen portion presses on the nerves and causes the accompanying pain. Many of our headaches and other pains are the result of accumulations of acid in certain parts of the body, which cause the flesh to swell and affect the nerves.

The increase in tenderness of proteins when hydrated in slightly acid solution is of importance in many phases of cookery. The addition of a little acid, such as vinegar or tomato juice, in cooking tough pieces of meat helps to make them more tender. Omelets and gelatin desserts are more tender if they are slightly acid. The addition of a base also increases the hydration of proteins,

but their peptizing action tends to disintegrate the proteins and makes them less attractive as foods. Salts have an effect opposite to that of acids and bases. Salts tend to become hydrated, and thus they dehydrate the colloids. In the study of the precipitation of colloids, it will be recalled that salts were used in high concentration for the purpose of dehydrating hydrophilic colloids to precipitate them. The salting-out of soap is an example. Alcohol also has a dehydrating action on hydrophilic colloids. We have referred to this in the use of alcohol to precipitate the pectin of fruit juices.

Wheat flour contains a protein called gluten. It is this protein that becomes hydrated in the mixing of batters and doughs. The hydrated gluten is elastic and allows the cake or bread to rise and to hold its shape when risen. The study of hydration illustrates the important results of the concentration of acids, bases, or salts on the texture of a baked product. Baking-powders contain different salts which tend to dehydrate the gluten and limit the stretching ability. Although the gas produced by the reaction of a baking-powder causes some lightness in the product, the dehydrated gluten prevents the best results from being obtained. The hydrogen ion concentration of a dough depends principally on the baking-powder which is used, or on the amount of baking-soda and sour milk added. At the same time, the sugar, salts, shortening, and egg each exert an influence on the batter. The simultaneous effects of dehydrating agents, protective colloids, and other factors make the problems of cake or biscuit baking quite complex.

Syneresis. **Syneresis** is the name given to the separation of hydrophilic gels into a thin liquid and a more solid gel; for example, the separation of sour milk into curds and whey, or the formation of a liquid from starch gels, gelatin gels, or custard. A gel structure, as previously described, appears to be firm but is an unstable arrangement of colloidal micelles packed together with a liquid phase (water or a dilute solution). After standing or after increased coagulation by heat, the structure may collapse, and the liquid material will then separate from the concentrated phase.

EMULSIONS

When one liquid is dispersed in another in which it is not soluble, it is said to be **emulsified**. Emulsions may be made by shaking together any two liquids that are not soluble in each other, such as kerosene and water. Such emulsions are not stable, and the liquids separate easily. A property of liquids, called surface

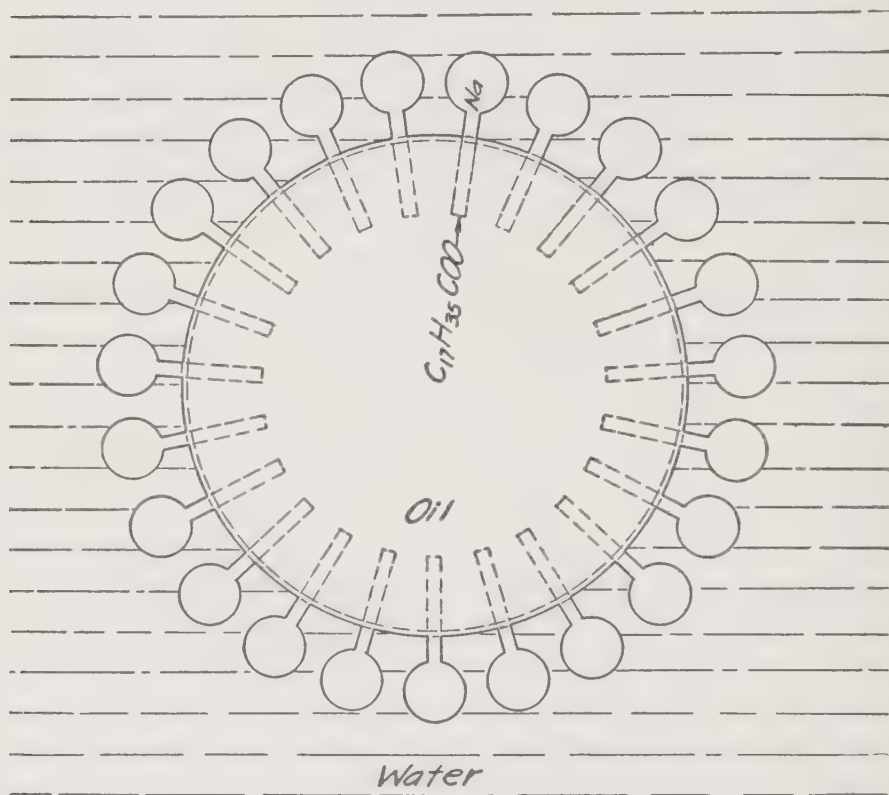


FIG. 42. Emulsion: Kerosene in Water Emulsified with Soap

tension, explains why two liquids insoluble in each other always form two layers. **Surface tension** means the tendency of a given amount of liquid to expose the least surface that is possible. Obviously, a liquid exposes more surface when dispersed in drops than when present as a continuous layer. In other words, the sur-

face area in an emulsion is many times that of the two liquids in separate layers. If the tension of each liquid is high, there will be a strong tendency for the colloidal droplets to unite and form two layers of liquid. To make an emulsion stable, a third substance must be added, called the **emulsifying agent**. This substance must either lower the surface tension, so that the tendency for the bubbles to break and unite into larger particles is small, or it must form a tough film around each droplet in the emulsion and thus prevent its breaking to form larger drops. The best emulsifying agents act in both ways. Soap, fine powders, and proteins of various types are common emulsifying agents.

The action of soap in stabilizing a kerosene-and-water emulsion illustrates a method by which many of the emulsifying agents may act. Soap consists of long, narrow molecules of the sodium salts of fatty acids. Fatty acids, as a rule, are quite soluble in kerosene and quite insoluble in water, while the sodium salts are usually soluble in water. When kerosene is added to a soap solution, the soap molecules become concentrated between the two layers of liquid, the sodium ends of each molecule being dissolved in the water, while the fatty acid ends are dissolved in kerosene. When the mixture is shaken to form an emulsion, each tiny drop of kerosene becomes coated with soap molecules, the fatty acid end in the oil and the sodium end in the water (Fig. 42). The film thus formed stabilizes the emulsion by preventing the drops of oil from uniting into larger drops. The action of soap as an emulsifying agent is an important factor in its cleansing ability. Besides adsorbing dirt, soap emulsifies grease or oils that cause dirt to stick to a fabric. The emulsification is aided by the rubbing and mixing that accompany washing. The emulsified grease and the dirt adsorbed by the soap may then be washed away.

All colloid chemists are interested in mayonnaise and French salad-dressings, because they are typical emulsions. In making mayonnaise, an egg yolk is beaten, and mustard and other powders may be mixed in as seasoning. Oil and vinegar are added slowly, and the mixture is beaten until the oil is in the form of droplets. The protein of the egg and the fine powders act as emulsifying agents, lowering the surface tension and forming

films around the droplets of oil, and thus make the emulsion stable.

French dressing does not have any protein added to stabilize the emulsion, and must depend on large quantities of mild-flavored powders as emulsifying agents. For this reason, the emulsion is more easily broken than in mayonnaise dressings. Some companies, however, prepare French dressings in stable form by the use of gelatin or some other effective protective colloid.

SUMMARY

Since colloid chemistry treats of our bodies, our foods, our clothing, and our shelter, it touches our everyday life more closely than any other study. It is a comparatively new science, for although colloids were described and studied as early as 1861, most of what we now know about them has been discovered since the ultramicroscope was first made in 1904. Everywhere research workers are studying this interesting subject in an effort to understand more clearly the properties of colloidal matter and its application to everyday problems. We can hope that this research will gradually make all the processes of cooking more definite and that it will give us a better conception of the structure of our bodies and of the treatment of them in disease.

QUESTIONS AND PROBLEMS

1. Give the physical state (gas, liquid, or solid) of the dispersed part and the dispersion medium in the colloids: pearls, jello, soap, tea, fog, gravy, whipped cream, ink, oil paint. Classify each colloid as sol or gel.
2. Name six methods for making **colloids**; briefly describe each method; give an example of one colloid made by each method.
3. What is the method by which the following colloids are prepared: oil paints, sulphur sol, gelatin jelly, ferric hydroxide sol, ice-cream.
4. Why should fudge be cooled before it is beaten? How does the addition of corn syrup help to make a creamy candy?
5. Explain how the following properties of colloids give an idea of the size of colloidal particles: (1) Tyndall effect; (2) dialysis; (3) rate of settling; (4) diffusion.

6. (a) List and briefly describe five general properties of colloids; in each case, state whether a solution and a precipitate shows the corresponding property.
(b) List and briefly describe four properties characteristic of gels.
7. Give two ways by which a protein colloid can acquire an electric charge.
8. Compare the ease by which hydrophobic and hydrophilic colloids are made into precipitates. Explain the relationship between the valence of the ion of an electrolyte and its precipitating power on a colloid. How are hydrophilic colloids precipitated?
9. What name or property describes the following phenomena:
 - (1) separation of sour milk into curds and whey
 - (2) cones of light from auto lights in a fog
 - (3) the pH value at which a hydrophilic colloid has no electric charge
 - (4) rapid movement of colloidal particles in a sol
 - (5) separation of electrolytes from colloidal matter in a sol by a membrane
 - (6) separation of electrolytes from colloidal matter by suction through a membrane
 - (7) individual colloidal particles
 - (8) concentration of a solute on the surface of colloidal particles
 - (9) substances insoluble in water colloiddally dispersed in water
 - (10) tendency of liquids to form in shapes that have a small surface
 - (11) a colloid that forms as a thin liquid
 - (12) preparation of colloidal particles by disintegration of precipitates
 - (13) adsorption of water by a hydrophilic colloid.
10. How does an egg white clarify muddy coffee?
11. How does boiling fruit juice before straining help to make a clear jelly?
12. Why does tomato juice tend to curdle milk? Should the addition of baking-soda prevent this? Could white sauce prevent it?
13. Why do deltas form where rivers empty into the sea?
14. Why does mayonnaise salad dressing form a more stable emulsion than French dressing? What are the two liquids insoluble in each other? What is the purpose of the egg and mustard?
15. What is the emulsifying agent in gravy? Would long cooking tend to break the emulsion and separate the fat?
16. Give two ways in which soap aids in cleansing.
17. Give two reasons for adding baking-soda to a bee sting.
18. Why is alcohol used to test the jelly-making properties of a juice?
19. Explain the following terms and give an example of each: dispersion medium, dispersed part, sol, gel, hydrophobic colloid, hydrophilic colloid, Tyndall effect, ultramicroscope, Brownian movement, ad-

sorption, dialysis, isoelectric point, syneresis, emulsion, surface tension, micelle, hydration, intermicellar liquid.

20. Tell how hydration in acid or basic solution and dehydration in the presence of salts affect the tenderness or toughness of protein in the following: (1) cooking of meats, (2) making gelatin jelly, (3) baking-powder in batters containing gluten.
21. Name the three parts of an emulsion and tell the purpose of each part. Give two ways in which an emulsifying agent affects the stability of an emulsion.
22. Give two examples of emulsions. What is the nature of the three components of each emulsion?

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CHAPTER XXXII

LEAVENING AGENTS

IN the olden days, when a housewife made a cake, she may have used no special leavening agent. Instead, the product was made light by the incorporation of air into the mixture by prolonged beating of the eggs and the fat. The steam that formed during the baking also had considerable leavening power. To-day most cake mixtures contain less fat and eggs, but some substance is added to the batter that will react to form a gas during the baking process. A substance which approaches the ideal leavening agent has no undesirable effect on the dough and leaves no taste in the baked product. The compound which is satisfactory in every respect is still to be discovered. The product usually formed by the leavening agent is carbon dioxide, an odorless, tasteless, and non-poisonous gas. It may be incorporated into the batter in several ways. Most living organisms evolve carbon dioxide as a product of respiration; also it is a product of the decomposition of many organic compounds and of a few inorganic compounds. Whenever a carbonate reacts with any acid, carbon dioxide gas is evolved. Of the numerous combinations that might be used for leavening, only a few have been found useful in baking. These are yeast, baking ammonia, baking-soda, and baking-powders.

YEAST

Yeast consists of a mass of the cells of certain microscopic organisms. When the organisms are in the form of a yeast-cake, they are in the dormant state. Under favorable conditions, the yeast organisms grow and reproduce. They use dextrose as a food, which in turn is decomposed into ethyl alcohol and carbon dioxide (Chapter XXIX). The reaction may be represented by the equation



The carbon dioxide is evolved only as fast as growth and reproduction of the yeast organism occurs. Leavening with yeast, then, is satisfactory only for bread or foods which are prepared some time before baking. This gives an opportunity for the organisms to develop. As the sugar is used, carbon dioxide forms and works its way through the dough, thus giving a leavening effect.

BAKING AMMONIA

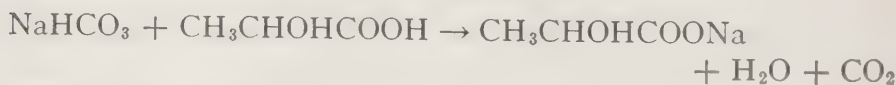
Baking ammonia, or ammonium bicarbonate, NH_4HCO_3 , has been used to a limited extent as a leavening agent in cookies and crackers. When heated this salt decomposes into ammonia, steam, and carbon dioxide — all gases. This makes ammonium bicarbonate an efficient leavening agent. The chief disadvantage in the use of this salt lies in the disagreeable flavor of the ammonia gas that may be left in the freshly baked product.

BAKING-SODA

Baking-soda is sodium bicarbonate, NaHCO_3 . When heated sufficiently this salt decomposes, evolving carbon dioxide gas as a product. The following equation indicates the chemical change:



The amount of carbon dioxide obtained by this reaction at baking temperature is too limited to be dependable as a source of the gas for leavening. Sodium bicarbonate may be used as a leavening agent, however, because it will react with any acid either at room temperature or at temperatures attained in baking, forming carbon dioxide as one of the products. The acid usually used is the lactic acid of sour milk. It is a weak acid, is wholesome, and is easily obtained in the home. The reaction that takes place when lactic acid is added to baking-soda is



Sodium lactate, a harmless organic salt with no undesirable flavor, is left as a residue in the baked food when this combination is used.

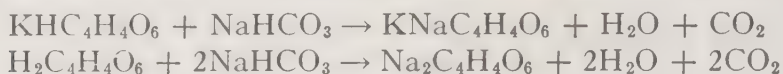
There is one serious disadvantage in the use of baking-soda and sour milk for leavening. Different samples of sour milk do not have the same acidity or sourness and hence require different amounts of baking-soda for neutralization. Both the baking-soda and the sodium lactate that is formed by the reaction give a basic solution when dissolved in water. Therefore if an excess of baking-soda is used, the batter will have a decided basic reaction. This not only gives an undesirable taste and a brown color to the product, but affects the texture also, by peptizing the gluten. An excess of acid (sour milk) is less harmful but may give a sour taste to the food. The uncertainty of results from the use of sour milk with varying pH value has made the method unpopular with modern cooks.

BAKING-POWDERS

The mixtures designated as baking-powders appeared on the market about 1850. They represented a new type of leavening agent consisting of a mixture of a solid acid salt with sodium bicarbonate. Because the ingredients were mixed in the proper proportion by the manufacturer, the amount of carbon dioxide evolved by a given quantity of baking-powder and the pH value of the batters or doughs made with it were always the same. This made the results more certain than those obtained with baking-soda and sour milk. As long as such a baking-powder was kept dry, no reaction occurred, but when it was dissolved in water or a batter, carbon dioxide was evolved through the ionic reaction between the two components. Because of the ease with which they were used and of the consistent results obtained with them, baking-powders have become increasingly popular in America. Most recipes for cakes and hot breads in our cook-books to-day call for baking-powder as the leavening agent. In a few European countries where changes have taken place more slowly, many of the cakes are still made with yeast and have a different texture from those familiar to us.

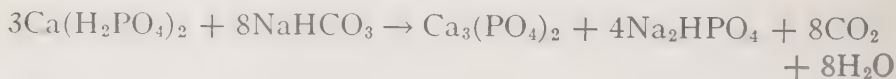
Reactions of Tartaric Acid and its Salts in Baking-Powder. — In the first baking-powders, cream of tartar, or potassium acid

tartrate, $\text{KHC}_4\text{H}_4\text{O}_6$, was used as the acid material to react with baking-soda. The potassium acid tartrate was obtained from France as large crystals recovered from the residue in wine-casks. The crystals were purified and powdered and were then mixed in the proper proportion with baking-soda and with enough starch or flour to keep the mixture dry. Tartaric acid, another crystalline compound, was often used with the cream of tartar. When such a baking-powder is added to water or a batter, allowing the ingredients to react, the following chemical reactions occur:



Tartaric acid is a relatively strong acid, and these reactions take place rapidly in cold water or in a batter at room temperature. If a batter in which this baking-powder is used as a leavening agent is allowed to stand before it is baked, or if it is baked too slowly, much of the carbon dioxide may be lost before the batter has coagulated sufficiently to hold its shape.

Reactions of Acid Phosphate in Baking-Powder. — Soon after the tartrate baking-powders began to be sold, an inexpensive method of preparing primary calcium phosphate from bone ash, $\text{Ca}_3(\text{PO}_4)_2$, and sulphuric acid was perfected. This compound then began to be used as an acid salt in place of the cream of tartar in some baking-powders. The reaction that occurs when this type of baking-powder dissolves in water or in a batter is:



This chemical reaction is a double decomposition similar to that in a tartrate baking-powder; consequently, the rate of reaction is rapid, and batters made with this type of baking-powder must be baked quickly.

Reactions of Sodium Aluminium Sulphate in Baking-Powder. — A third type of baking-powder soon devised used anhydrous or burnt alum, $\text{KAl}(\text{SO}_4)_2$, as the acid-reacting material. Later

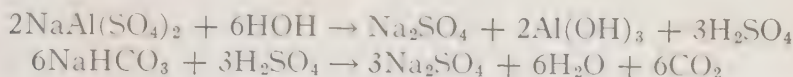


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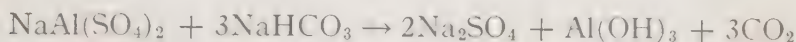
THE EFFECT OF EXTENT OF MIXING UPON THE VOLUME AND TEXTURE OF CAKES

These pictures show the effect of extent of mixing upon the volume and texture of cakes, both when a phosphate baking-powder is used and when an S.A.S. baking-powder is used. The same quantity of batter, 150 g., is baked in each cake. The three cakes at the left were made with phosphate baking-powder; reading from the top of the picture to the bottom, cake 1 was baked after beating 50 strokes, cake 2 was baked after beating 150 strokes, and cake 3 was baked after beating 1,000 strokes. The three cakes at the right were made with S.A.S. baking-powder. Cake 1, reading from the top of the picture to the bottom, was baked after beating 50 strokes, cake 2 was baked after beating 300 strokes, and cake 3 was baked after beating 1,000 strokes.

sodium aluminium sulphate became less expensive and replaced the potassium salt. Although these are not acid salts, they hydrolyze in water to give an acid reaction and thus bring about the evolution of carbon dioxide gas from the baking-soda. The reactions may be written as follows:



In the form of one equation, the reaction is the following:



A sodium aluminium sulphate baking-powder acts slowly at room temperature. This makes it possible and even desirable to allow batters made with this type of baking-powder to stand for some time before baking. Powders of this type are designated as S.A.S. baking-powders from the initial letters of their acid-reacting constituent, sodium aluminium sulphate.

Baking-Powder To-Day. — Under authority of the Pure Food and Drugs Act, the United States Department of Agriculture in 1918 formulated a concise definition to describe the baking-powders used to-day, as follows:

Baking-powder is the leavening agent produced by the mixing of an acid-reacting material and sodium bicarbonate, with or without starch or flour. It yields not less than twelve per cent (12%) of available carbon dioxide.

The acid-reacting materials in baking-powder are (1) tartaric acid or its acid salts, (2) acid salts of phosphoric acid, (3) compounds of aluminium, or (4) any combination in substantial proportions of the foregoing.

This standard recognizes the materials most commonly used in baking-powder. It limits the amount of starch and other inert material that may be added to a baking-powder and ensures that the leavening ability of different baking-powders will be nearly the same. Practically all baking-powders on the market to-day have at least 14 per cent of available carbon dioxide. Because the laws of several States require it, the ingredients of baking-

powders are generally printed on the labels. This makes it possible for the purchaser to know the composition of any brand.

Types of Baking-Powders. — All baking-powders have the same composition except for the acid-reacting material used, so this constituent is the logical basis for classifying them. On this basis, the three chief types of baking-powder on the market to-day are:

1. *Tartrate Baking-Powders.* These contain cream of tartar alone, or a mixture of cream of tartar and tartaric acid, as acid-reacting materials.

2. *Phosphate Baking-Powders.* These usually contain primary calcium phosphate as the acid-reacting constituent. Primary sodium phosphate is used in some baking-powders prepared for the bakeries.

3. *Combination Baking-Powders.* These use a mixture of primary calcium phosphate and sodium aluminium sulphate as acid-reacting material.

We have noted in a study of baking-powder reactions that the first two baking-powders mentioned are rapid-acting types. When a combination baking-powder is added to a batter, the reactions given for phosphate and for S.A.S. baking-powders take place, as well as a partial reaction between the phosphate and the sodium aluminium sulphate. The two acid-reacting materials result in a double action, since the phosphate reacts with the baking-soda to evolve some carbon dioxide in the cold batter, and the sodium aluminium sulphate reacts to form more carbon dioxide under the influence of the heat of the oven. This type of baking-powder is useful in bakeries, where batters or doughs often stand for some time before baking. It is popular also with people who are learning to cook and who work slowly. If an excess of this type of baking-powder is used, the sodium aluminium sulphate may give an undesirable taste to the product. On the other hand, because it is more efficient, it can be used in smaller quantities than the other types.

Residues. — A study of baking-powders would not be complete without some attention being given to the residues left in the

baked product. All the original ingredients of the powder, except starch, are completely changed through chemical reaction into other substances, one of which is the desired carbon dioxide gas. In some of the reactions, water is formed. The other products of the reaction remain in the cooked food. The reaction for tartrate baking-powder produces either sodium tartrate or potassium sodium tartrate (Rochelle salts) or both. Calcium phosphate and disodium phosphate are formed from phosphate baking-powder, while with S.A.S. baking-powder the residues left are sodium sulphate and aluminium hydroxide. All of these residues affect the texture of the baked product to a surprising extent.

Tartrate baking-powders are more expensive than phosphate or S.A.S. baking-powders because of the greater expense involved in obtaining cream of tartar. Therefore, in order to compete with other companies, the manufacturers of tartrate baking-powder have attempted to prove that the residues left from their baking-powder are more wholesome than residues from the other types. Scientists have studied the effect of feeding comparatively large amounts of the various residues not only to animals such as rats and dogs, but also, over extended periods of time, to man. The general opinion to-day is that, although large quantities of the residues from any type of baking-powder have a cathartic action, the amount taken in the ordinary diet is too small to have any effect. If hot breads should form a large part of the diet, however, this cathartic effect might be produced.

QUESTIONS AND PROBLEMS

1. Write an equation for the decomposition of sugar by the action of yeast. Why does the leavening process take so much longer when yeast is used?
2. Write the equation for the decomposition of baking-soda and of ammonium acid carbonate when heated. How many cubic centimeters of carbon dioxide would be evolved by heating five grams of each compound? What other useful gases are evolved?
3. How many cubic centimeters of gas would be evolved by the complete reaction of five grams of baking-soda with lactic acid? with cream of tartar? with calcium acid phosphate? with sodium aluminium sulphate?
4. What is the disadvantage of using baking-soda and sour milk? Can you think of any advantage?

5. If you wished to make up a baking-powder mixture using one teaspoon (five grams) of baking-soda, how many grams of cream of tartar would be used?
6. Give formulas and names of the residues left in the food when each type of baking-powder is used. Would you expect the residues to have an effect on a batter? Explain your answer.
7. Tabulate a comparison of tartrate, sodium aluminium sulphate, and phosphate baking-powders according to the rate of reaction, residues left in the food, healthfulness, cost, and taste.
8. What are the advantages of combination baking-powders?

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CHAPTER XXXIII

WATER AND ITS USES

WATER is used in an unlimited number of ways in the laboratory, in the home, and in industry. The practical chemist is interested in the substances dissolved in water as well as the effect of these substances upon its use. Water is an excellent solvent, and when found in nature it always contains several impurities in solution. It is fortunate that chemically pure water is usually not necessary and often not desirable.

The various types of water may be classified according to the source and the impurities characteristic of each source. Rain-water, when it reaches the earth, is saturated with nitrogen and oxygen and contains carbon dioxide, ammonia, and possibly other compounds in solution, together with dust and micro-organisms in suspension. Snow, because of its large surface area, carries more dust and micro-organisms than rain. A study of the composition of the rain and snow falling at Mount Vernon, Iowa, during eight months showed that the precipitation added to each acre of land 2.035 lb. of chlorine, 0.57 lb. of sulphur, and 3.93 lb. of nitrogen.

A large proportion of rain-water soaks into the ground and, in filtering through the soil, loses many of its impurities, especially micro-organisms and gases, but dissolves mineral matter. When this water is obtained from springs or wells, it is called hard or soft water, alkali or mineral water, depending on the type of soil it has passed through and the substances it has dissolved. If, instead of soaking through the earth, the water collects in rivers or lakes, it dissolves less mineral matter but more organic matter, giving micro-organisms an opportunity to grow. This is usually called surface water.

Spring or well-water is preferable for drinking. The mineral matter it contains improves the taste, and filtration through the soil usually removes any disease-producing micro-organisms that

may have been in suspension. On the other hand, mineral matter is undesirable when water is to be used in industry or in the laundry. The requirements of a drinking water and of an industrial water are so different that we may study them under separate headings.

DRINKING WATER

A satisfactory drinking water should be clear and sparkling, free from undesirable tastes and odors, and from disease-producing micro-organisms. The chemist is less important than the bacteriologist in determining the safety of a drinking water, since micro-organisms found in water are liable to be more harmful than the substances for which the chemist analyzes. When gases such as oxygen and carbon dioxide are in solution, they help to give the water a pleasant taste and a sparkling appearance. Inorganic salts in the usual small concentration found in hard water affect the taste slightly. The salts may affect the healthfulness of the water in different ways; for example, research indicates that traces of iodides in water have a tendency to reduce the prevalence of goiter, while traces of fluorides cause "mottled enamel" in the teeth of children using the water. A frequent danger the chemist may detect is the presence of poisonous lead or copper salts dissolved from storage tanks or distribution pipes. The most important factor to be considered in any drinking water is the possibility of contamination with decomposing organic matter or disease-producing micro-organisms. A few of the products of decomposition are poisonous in themselves; others indicate the possibility of the presence of disease-producing bacteria, since they occur only in water contaminated with animal refuse. A bacteriological analysis can determine whether or not harmful bacteria are present.

When water is obtained from wells over 100 feet deep, organic matter and micro-organisms have usually been adsorbed by the soil. Such a water is safe to drink. When water is obtained from rivers, lakes, or shallow wells, there is danger of contamination and the water must be treated or purified before it is safe to drink. When a turbid or muddy river is used by a city as a source of

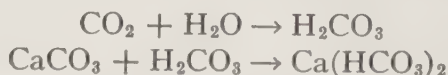
drinking water, the water is stored in large reservoirs for some time before further treatment, in order that the mud may settle. In Omaha, Nebraska, where water is taken from the Missouri River, several feet of mud may form in the settling tanks in twenty-four hours. It has been observed, also, that storage reduces the number of bacteria in the water. Often the turbidity of river water is caused by colloidal matter that will not settle on standing. In such cases, some salt must be added to coagulate the colloids. Ferrous sulphate (readily oxidized to ferric sulphate), aluminium sulphate, and sodium aluminate are used. These salts contain trivalent ions, which are most effective as precipitating agents (Chapter XXXI). If aluminium or iron sulphate is used, the coagulation is hastened by adding slaked lime, $\text{Ca}(\text{OH})_2$, to adjust the hydrogen ion concentration of the water to the $p\text{H}$ value at which the aluminium or iron hydroxides are most insoluble. The gelatinous precipitate adsorbs the colloidal silt and in settling carries other impurities with it.

After clarification with salts, the water may be filtered through layers of fine sand, then through coarse gravel; the filtration removes the precipitate of aluminium hydroxide and other impurities from the water. After this treatment the water is usually free from turbidity, color, and odor. In a few places, it is further treated by aëration. In this process compounds with offensive odors are oxidized, bacteria are killed, and the water is made more clear and sparkling by the dissolved air. To make more certain that the water is safe to drink it may be given a final sterilization treatment. Chlorine, sodium hypochlorite, bleaching-powder, and ozone are used as sterilizing agents. Chlorine has been demonstrated to be especially effective and is easily added to large supplies of water. Bleaching-powder and sodium hypochlorite are more easily added to small supplies of water and owe their bactericidal properties to the oxidizing action of the hypochlorous acid present. Ozone is an active oxidizing agent and in this way acts as a bactericide.

HARD WATER

As water seeps through the soil, soluble inorganic salts dissolve which may give to it the properties characteristic of hard water. The salts that are most troublesome in this respect are those of calcium, magnesium, and iron. Because of the many undesirable effects of these ions in the laundry, in steam boilers, and in industrial uses, their precipitation and removal is one of the important problems in the chemistry of water.

Calcium and magnesium occur in the soil as the insoluble carbonates. Calcium carbonate is best known as limestone or marble. Magnesium carbonate is often found combined with the calcium carbonate as $\text{CaCO}_3 \cdot \text{MgCO}_3$. The acid carbonates corresponding to these salts, $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$, are soluble. As rain-water containing carbon dioxide in solution passes over the normal carbonates, the soluble acid carbonates form and dissolve, forming hard water. This is shown by the following equations:



As the water continues to dissolve the limestone beds, underground caves may be formed. Many famous caves owe their origin to this chemical reaction.

The reaction given for the formation of calcium acid carbonate in solution is reversible. According to the mass law, the speed of a reaction depends on the molecular concentration of the reacting substances; so too, it is evident that concentration of calcium acid carbonate in solution is dependent on concentration of carbon dioxide. If carbon dioxide is removed from water by heating it or by reducing the pressure on it, the reaction is reversed and normal calcium carbonate precipitates. This explains the deposit of calcium carbonate formed in tea-kettles in which hard water is heated. Calcium ions are removed from the water by the formation of calcium carbonate, a precipitate, and the water is said to be softened. The removal of iron and magnesium carbonates from solution by heating is incomplete because these carbonates are more soluble than calcium carbonate.

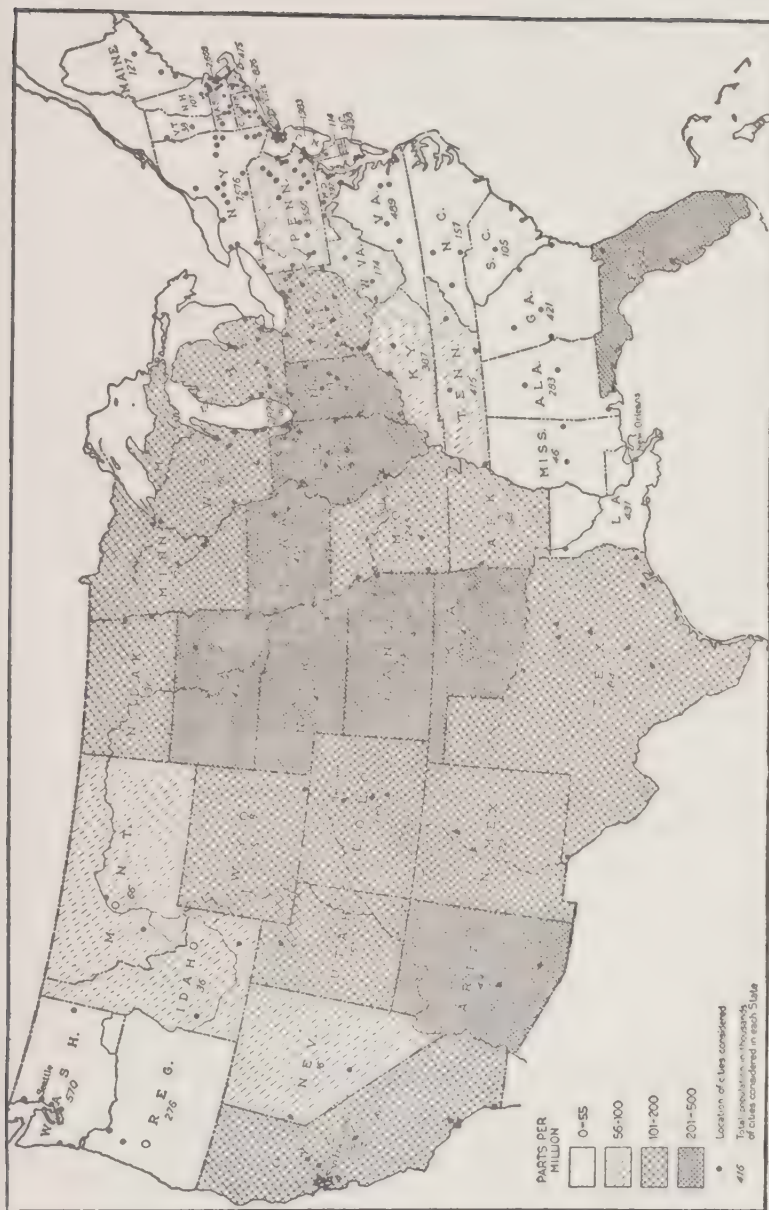
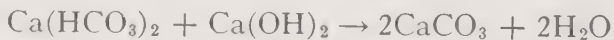


FIG. 43. Average Hardness, by States, of Water Furnished by Public Supply Systems in Over 300 Cities in the United States; also Population, by States, of the Cities Considered. From United States Geological Survey, *Water-Supply*, Paper 496.

The Softening of Water. — The presence of acid carbonates alone, such as calcium acid carbonate, $\text{Ca}(\text{HCO}_3)_2$, or magnesium acid carbonate, $\text{Mg}(\text{HCO}_3)_2$, is known as **temporary hardness** in water. As just stated, these salts are decomposed by heat and the normal carbonates are precipitated. Thus, water containing these salts may be softened by heating. In many cases, calcium and magnesium are in solution as sulphates or chlorides. When these salts are present, the water cannot be softened by heating, and chemical methods are necessary. Salts such as magnesium sulphate, calcium sulphate, magnesium chloride, and calcium chloride are said to cause **permanent hardness** in water. Hard water may contain both types of salts, and for practical purposes water is usually softened by chemical methods. There are three general chemical methods for water-softening in use to-day.

The Lime-Soda Process. The lime-soda process is used when large volumes of water are to be softened. In many cities the municipal supply is softened by this process; and when railroad companies have found it profitable to soften the water used in locomotives, this method has been found advisable. The addition of slaked lime, $\text{Ca}(\text{OH})_2$, and washing-soda, Na_2CO_3 , precipitates most of the calcium salts as the carbonate, and the magnesium salts as the hydroxide. Although calcium compounds in excess cause hardness of water, calcium hydroxide, a base, may neutralize the acid carbonates, forming the insoluble normal salts. This is shown by the equations:



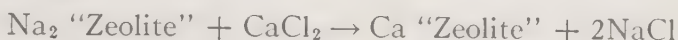
Washing-soda reacts with the salts that cause permanent hardness and with the excess calcium hydroxide to form insoluble salts. Using the sulphates as typical, these reactions may be written:



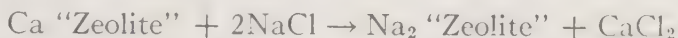
In this process water is softened by adding the inexpensive substances slaked lime and washing-soda and allowing the precipitate to settle. Alum may be added to the water. Hydrolysis occurs,

forming aluminium hydroxide, a flocculent precipitate which settles quickly, carrying with it the calcium and magnesium precipitates and any other suspended matter.

The "Zeolite" Method. The modern water-softening device used in the home and in industries contains a chemical sold under such trade names as "Zeolite" and "Permutite." This chemical is composed of complex insoluble sodium alumino-silicates, of which a typical formula is $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{Na}_2\text{O}$. As hard water filters through sodium "Zeolite," the latter gradually changes into calcium "Zeolite." The reaction may be represented by the equation:



When this reaction has taken place, water filtering through the calcium "Zeolite" is not softened. The "Zeolite" may be regenerated by allowing a concentrated solution of salt (sodium chloride) to remain in contact with it for a few hours. Calcium "Zeolite" reacts with sodium chloride as indicated by the equation (the reverse of the one just given):

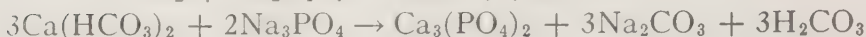
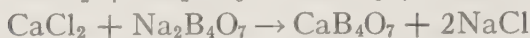
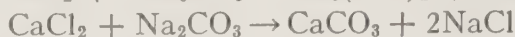


By this reaction the "Zeolite" is regenerated and becomes useful again as a chemical in the water-softener.

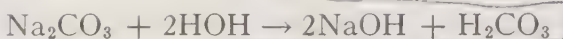
The softening power of a "Zeolite" water-softener does not depend entirely upon its size, since some "Zeolites" are more porous than others and expose more surface to the hard water. The calcium and magnesium salts causing permanent and temporary hardness of water are removed in one operation by the "Zeolite" method. Sodium ions are added to the water, but in this concentration they are not as objectionable as calcium and magnesium ions.

Washing-Powders. The easiest, yet the most expensive, method for softening water in the home is by the addition of washing-powders. Most washing-powders and bath-salts contain mixtures of sodium salts of weak acids. The more common salts used are trisodium phosphate, Na_3PO_4 , sodium carbonate, Na_2CO_3 , and sodium pyroborate, or borax, $\text{Na}_2\text{B}_4\text{O}_7$. Sand and soap may be added to the washing-powder to aid in the cleansing.

These salts soften the water by reacting with the calcium and magnesium ions to form insoluble salts. The following equations show the reaction:



The sodium salts used in washing-powders hydrolyze in water to give a basic reaction. This may be illustrated by the equation

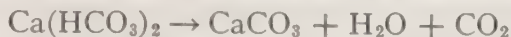


In cleaning greasy articles, the slightly basic solution reacts with the fat, forming a soap. The cleansing effect of washing-powders, then, consists of both types of reaction just indicated — the softening of the water and the removal of grease by means of the basic reaction. Washing-soda should be used in limited amounts (not excess) because the sodium hydroxide formed by hydrolysis tends to peptize protein, and so it will harm the skin as well as some textiles (Chapter XXXIV).

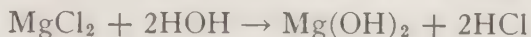
A mixture of sodium silicate (water-glass) and sodium hexametaphosphate (NaPO_3)₆ with the other ingredients of washing-powder makes a product that is desirable for use on metal utensils and dishes. The water-glass softens the water and, because of its jelly-like, colloidal consistency, is less harmful with aluminium and zinc than other washing-powders. The sodium hexametaphosphate also softens the water and is valuable because it leaves no film on dishes when they are washed in hard water.

The Advantages of Softened Water. — The removal of salts causing hardness of water has been a great help in factories and in most of the industries. The use of softened water in steam boilers eliminates the boiler-scale so prevalent when hard water is heated. Boiler-scale consists of the compounds calcium carbonate, CaCO_3 , magnesium carbonate, MgCO_3 , magnesium hydroxide, $\text{Mg}(\text{OH})_2$, and calcium sulphate, CaSO_4 . Calcium and

magnesium carbonates are formed when the corresponding acid salts in the water are heated, as shown by the equation

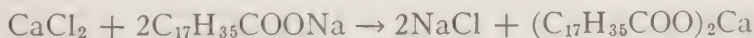


Magnesium hydroxide is insoluble and forms as the magnesium salts in the water undergo hydrolysis, as shown by the equation



Calcium sulphate is less soluble in hot water than in cold water and thus forms as a precipitate when hard water containing it is heated. The scale formed by the precipitation of these salts is a hard, porcelaine-like substance that prevents the conduction of heat into the boiler and fills up the pipes so that they cannot carry water. The American Railway Engineers Association has calculated that softening water used by the railroads in some communities saves as much as \$8,000 a year on each locomotive.

The effect of calcium compounds on soap is especially undesirable in laundries. Soap is a gel consisting of the sodium salts of fatty acids. It may either be dissolved or be colloiddally dispersed in the water. Soap cleanses by emulsifying and adsorbing the grease and dirt. If calcium and magnesium salts are dissolved in traces in the water, they react with soap to form insoluble calcium and magnesium soaps which precipitate as a greasy layer on the surface of the water. The formation of a calcium soap is shown by the equation:



The precipitate formed has no emulsifying properties and no cleansing action. After all of the calcium and magnesium salts have been precipitated, any excess of soap will act the same as in soft water. Water then may be softened by the addition of soap, but the method is expensive and the precipitate formed clings to articles and gives them a grayish color.

The use of soft water has several important advantages in industry. In canneries it has been found that the calcium and magnesium salts in hard water hinder the softening of peas and beans and the calcium salts precipitate as calcium oxalate when vegetables containing oxalic acid are canned. Coffee and tea are hy-

drophobic colloids, and the salts in hard water tend to make them cloudy. In the dyeing of textiles, the salts in hard water occasionally react with the dyes, giving unexpected results.

All of these difficulties are met on a smaller scale in the home. Boiler-scale forms in tea-kettles, making them heavy and inefficient. Hard water may cause disappointing results if used in cooking peas or beans or in making tea or coffee. In the laundry, calcium salts waste soap and make cleaning difficult. It has been estimated that the city of St. Louis, by partially softening its city water, saves the inhabitants \$920 worth of soap a day, and that in the city of Columbus, Ohio, softening of city water saves the average family sixty-three pounds of soap a year.

QUESTIONS AND PROBLEMS

1. What impurities make surface water undesirable for drinking? What impurities make well water undesirable for industrial purposes (laundries and factories)?
2. Describe the processes used in purifying drinking water. What methods would be applicable to camp life?
3. List the formulas and names of salts causing temporary hardness of water; the salts causing permanent hardness of water.
4. Write equations for the formation in nature of a salt that causes temporary hardness of water.
5. Write equations to illustrate the following methods of softening water:
 - (1) the reaction of slaked lime with a salt causing temporary hardness of water
 - (2) the reaction of washing-soda with a salt causing permanent hardness of water
 - (3) the action of heat on a salt causing temporary hardness of water
 - (4) the reaction of "Zeolite" with a salt causing permanent hardness of water
 - (5) the reaction of normal sodium phosphate with a salt causing permanent hardness of water.
6. Describe the method of regenerating "Zeolite" that has been used to soften water. Write an equation for the reaction.
7. Give formulas and names for three compounds usually found in boiler-scale. How is each of the compounds formed from the salts present in hard water?
8. Write an equation to illustrate the reaction of soap with a salt present in hard water.
9. Give some advantages in the household use of softened water.

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CHAPTER XXXIV

CHEMISTRY IN THE LAUNDRY

In the preceding chapters, several references have been made to the chemistry of cleaning processes. The chemistry of hard water, of soaps, and of bleaching-powder has been discussed. The reaction of these upon a textile fiber cannot be studied without a knowledge of the chemical composition of the textile. Moreover, these same cleansing agents may react with the dyes that are a part of the fabric, and it is therefore important to study the composition and chemical properties of the dyes also.

Types of Textiles. — The most familiar textile fibers may be classified into three groups: animal or protein fibers, plant or cellulose fibers, and the synthetic fibers.

In primitive times clothing consisted of the skins of animals; later the hairs of animals were matted into a felt from which clothing was made. Still later, the hairs were woven into a cloth. The weaver discovered that wool hairs gave a fine, soft yarn, and hence these hairs became more popular than other hairs. When wool fibers are observed under a microscope, they appear like slender tubes made of scales closely packed together (Fig. 44). Air imprisoned by these scales helps to prevent the conduction of heat. That is, a woollen garment does not conduct heat from the body, and hence it gives a feeling of warmth. When wool is exposed to the action of hot water or of alkaline solutions, the scales of the fiber tend to protrude and interlock. This shortens the fibers and causes a shrinkage of the fabric. Wool fibers are dissolved by solutions of sodium hydroxide.

Silk textiles were introduced to Europe from China and Japan. The natives of these countries learned to unwind the fiber from the cocoons spun by the silkworm. They found a method for washing the gum from the fiber, leaving a soft, lustrous filament.

They learned, also, to cultivate the silkworms that spun the best and finest fibers. Under the microscope, silk fibers look like long, slender tubes with a smooth surface (Fig. 44). It is the reflection of light from this smooth surface that explains the luster and sheen of silk fabrics.

Silk and wool are protein in nature. Like other proteins, the fibers are amphoteric; they are positively charged in acid solution and negatively charged in basic solution. These fibers are peptized and weakened by contact with dilute solutions of a base. Wool is completely dissolved by boiling in 10 per cent sodium hydroxide solution. Silk, also, is dissolved by treatment with sodium hydroxide. When wool and silk fibers are burned, there is an odor characteristic of the burning of any protein material. The burning test is a simple method for distinguishing animal fibers from other types.

The chief plant fibers are linen and cotton. Linen fibers are obtained from the inner part of the stem of the flax plant. The Egyptians learned to soak these stems in water so that the fibers could be pulled apart into threads. The fibers vary in length from a few inches to several feet. Under the microscope, linen fibers appear to consist of slender tubes with a smooth surface; at intervals, the fiber has cross walls or nodes similar to those in bamboo stems (Fig. 44). Except for the nodes, linen and silk fibers appear much alike, but it is always possible to distinguish between them by means of a microscopical examination. Both are smooth fibers and so have a luster. Linen and silk fibers are not flexible and so may crack in places where they are constantly pressed in folds. Linen has the property of absorbing moisture more readily than any other textile. This property makes linen especially desirable for toweling and for bandages.

Cotton fibers consist of the seed-hairs of the cotton-plant. These seed-hairs may be from 0.4 to 1.5 inches in length. Under the microscope, they appear as flat, twisted tubes (Fig. 44). Because of the twist, it is easy to spin cotton fibers into threads. Cotton and linen have a greater heat conductivity than wool fibers; that is, they conduct heat from the body and thus have a cooling effect.

Mercerized cotton is made by treating cotton fibers with concentrated sodium hydroxide. The cellulose of the cotton reacts with the alkali to form an unstable compound which, with water, gives cellulose hydrate. If the fibers are held under tension dur-

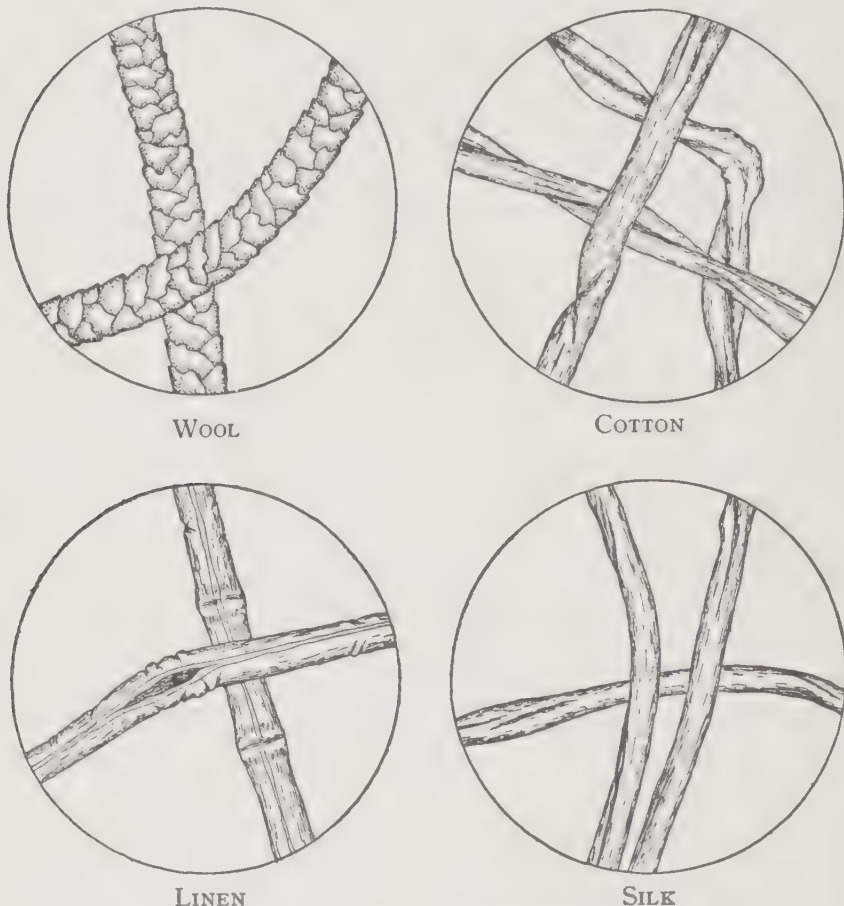


FIG. 44. Textile Fibers as They Appear under the Microscope

ing the treatment with sodium hydroxide, they lose their twist and swell to a cylindrical shape. The inner portion of the fibers becomes gelatinous and translucent. These smooth-surfaced fibers reflect light and thus give a luster to fabrics prepared from them. Mercerized fibers have a higher tensile strength than un-

treated cotton fibers. They have been used extensively since 1890, but are now being replaced by synthetic fibers.

Synthetic fibers which resemble silk are prepared from inexpensive forms of cellulose such as cotton linters, spruce wood, and corn-stalks. While the method for manufacturing these fibers has been developed in recent years, French scientists have been at work on the problem since 1754. In 1884, a French scientist took out the first patent on a process for the manufacture of artificial silk. Since that time, patents have rapidly followed until synthetic fibers are prepared that rival natural fibers in beauty of texture, in strength, and in wearing qualities.

Synthetic Fibers. — **Rayon** may be called a semi-synthetic fiber; it is not synthesized directly but is formed from plant material by dissolving the cellulose in some reagent and then reprecipitating it in the form of smooth filaments. The tubes or filaments may be fine or coarse, depending on the diameter; in turn the fiber spun from fine filaments may have a different texture than that spun from coarse filaments. The diameter of the filaments depends on the mechanical precipitation of the cellulose. In other words, the mechanical engineer or the inventor has been as necessary as the chemist in the successful development of manufacturing methods for these fibers. Four types of reactions have been used to make the rayons.

The **nitrocellulose method** was the first process to be developed, but other processes have supplanted it. When cellulose is treated with a mixture of nitric and sulphuric acids, nitrate groups react with the cellulose to form nitrocellulose — a compound which is explosive and inflammable. Nitrocellulose is dissolved in a mixture of alcohol and ether, and the solution is forced through tiny orifices. While the long filaments are forming, the mixture of alcohol and ether evaporates. The product is a long, lustrous fiber composed of nitrocellulose. In order to render the fibers less inflammable, they are passed through a reducing bath in which the nitrate groups are removed; the composition of the fiber is then cellulose.

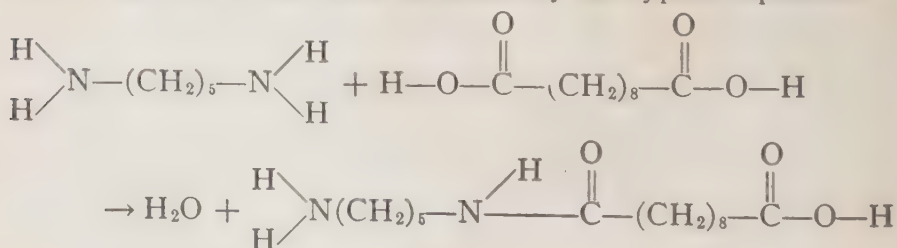
In the **cuprammonium method**, a concentrated solution of

copper sulphate and ammonium hydroxide is used to dissolve the cellulose. The solution is forced through tiny orifices. As the filaments are formed, they pass into a precipitating solution which may be dilute sulphuric acid. After thorough rinsing, the filament is in the form of a long, soft fiber of the composition of cellulose.

The **viscose method** is based on the disintegration of cellulose by sodium hydroxide, and the solution of this substance in carbon disulphide which forms a brown, viscous liquid. It is forced through tiny orifices into a dilute acid solution, and the filaments thus formed are spun into threads. The product is known as **viscose rayon**.

The **cellulose acetate method** depends upon a reaction between cellulose and acetic acid to form cellulose acetate (similar to cellulose nitrate), and the solution of it in acetone. The liquid forms filaments from which the acetone evaporates. The silky thread is woven into a textile called **celanese**. The fiber is not cellulose in composition, as are the other rayons, but a compound — **cellulose acetate**. It follows that the properties of celanese are not like those of other fibers; it dissolves in organic solvents that do not affect cellulose, it is resistant to water, and it can be dyed only with a special type of dye.

Nylon is a truly synthetic material, built up from the well-known materials — coal, air, and water. Nitrogen (from the air) combines with hydrogen (from water) to form ammonia; through a series of reactions, ammonia combines with carbon compounds to form complex molecules with long chains of carbon atoms linked together. Research showed that the elasticity needed for a silk-like fiber could be attained only from molecules that have active groups at either end, so that combination will take place to form long chain compounds, as shown by the typical equation:





Courtesy of Science Service, Inc.

GLASS FIBERS

Resting on the cloth of glass is the crude block of glass from which are made the fibers that go into glass yarn and thread. The yarns are woven into cloth in the ordinary fashion to make fireproof theater curtains and upholstery.

The product of the reaction still shows reactive amino, —NH_2 ,



and carboxyl, —C—O—H , groups which will combine with other molecules to form a chain of protein-like compounds. By a reaction of this type, molecules are formed which may be pulled or oriented the length of the material, and thus make a strong elastic filament for spinning and weaving. Nylon is in the process of adaptation for a variety of uses — hosiery, bristles in brushes, for parachutes, dresses, and lace.

Vinyon fibers are synthesized from a carbon compound quite different from that used for nylon, and consequently the properties are different. Textiles made from vinyon are resistant to water, acids, and bases; they do not conduct electricity and do not crease. They are used for filters for laboratory purposes, for fish-lines, nets, and seines, for shower curtains, bathing suits, and waterproof clothing.

Fibers made from milk-casein resemble wool. The casein is dissolved in lye and treated with formaldehyde to reprecipitate and harden the material. Similar fibers have been made from the proteins of soybean and fish.

Glass fibers may be spun and woven into textiles that are of value because they do not conduct electricity, and are resistant to fire, water, mildew, and chemicals.

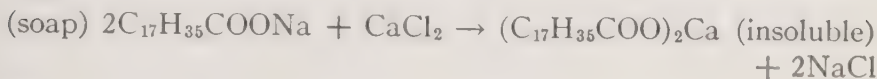
Tests for Textile Fibers. — It is often desirable to be able to distinguish between textile fibers or to determine the composition of some unknown fabric. It may be necessary to know the nature of a fabric in order to determine the treatment which it should be given in the laundry. The recognition of a fiber may be made by a microscopic examination, since each fiber has a characteristic structure (Fig. 44). In the home, animal fibers may be distinguished from cellulose fibers by the odor emitted while burning. The plant fibers and the rayons, except celanese, burn with an odor similar to burning paper, while the burning of silk or wool fibers gives an odor characteristic of the burning of protein matter. Another useful test is made with nitric acid. Protein fibers

are colored a bright yellow by concentrated nitric acid, while cellulose fibers do not change color but are disintegrated by this treatment. In a mixed fabric, the proportion of animal fibers may be determined by dissolving the protein from a piece of the fabric with a solution of sodium hydroxide. This may be done quantitatively by weighing the sample to be tested before and after the treatment with alkali. One may estimate the amount of protein fiber in a piece of mixed goods by comparing the appearance of a sample before and after the treatment with alkali.

Weighting of Textiles. — When certain salts are incorporated with textiles to enhance their appearance, the fabric is said to be **weighted**. A variety of properties may be given to fabrics by the use of different salt mixtures. The textile may be made more lustrous, and it may be made to appear firmer and smoother. The compounds may be held loosely by the fabric, or they may combine with it. Salts of iron and tin combine with silk fibers. A silk that contains one fourth of its weight or less of these salts is greatly improved in appearance and does not suffer in strength or wearing ability. Cheaper silks may be weighted much more than this amount, with the result that the fibers become less flexible and more easily broken, especially where the material is creased. Wool and cotton fabrics may be weighted with magnesium salts. Many fabrics are coated with a dressing or finish which is not permanent but improves the appearance of the fabric while it is new. Starch dressing is used on cotton sheets and dress-goods to make them look heavier. Gelatin, dextrin, and glue are added to stiffen certain fabrics. A moderate amount of dressing is an advantage because it makes the goods heavy and firm. They are thus kept in a better condition while passing from the factory to the consumer.

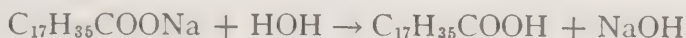
Cleaning Textile Fibers. — When textiles are laundered in the usual manner, they may be affected by hardness of water, by alkalinity of soaps or washing-powders, and by bleaching agents which are often used. When soaps are used with hard water, a

precipitate of the calcium or magnesium soap is formed. The reaction may be shown as follows:



This insoluble calcium or magnesium soap is a gray, gummy precipitate which settles on the fabric. Of course, the formation of this precipitate can be prevented by the use of softened water in which the calcium and magnesium salts are not present.

Soap is valuable in cleaning because of two colloidal properties: its ability to adsorb and its ability to act as an emulsifying agent. All soaps are alkaline in reaction because they react with water to form a strong base and a weak acid. This may be illustrated by the equation

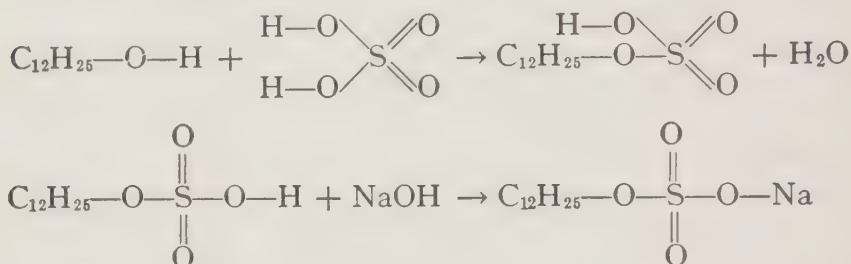


Soaps may be more alkaline than this reaction indicates. They are manufactured by the reaction of a fat with sodium hydroxide (Chapter XXIX). Unless the manufacturer is careful to remove the excess of sodium hydroxide, some of it may be dissolved in the soap mixture. Consequently, the alkalinity varies with the purity of the soap. A soap that is slightly alkaline may be used to advantage in laundering cotton garments. The dirt on such a fabric is thought to be held there by a film of oil or fat. An alkaline soap furnishes a limited amount of sodium hydroxide, which combines with this oil or fat and so removes it with the dirt. On the other hand, wool, silk, and some of the synthetic fibers are weakened by the alkaline reaction of soaps and washing-powders. Hence, a neutral soap should be used in laundering these fabrics.

The sodium salts of the solid fats form a hard soap (Chapter XXIX). This type of soap is not effective in cold water but has colloidal properties and cleansing ability in hot water. Soap chips are prepared from a solid soap and should usually be dissolved in hot water. The sodium salts of the vegetable oils make a soap that has a smooth, soft texture; it has colloidal properties in cold water but forms a true solution in hot water. That is, its adsorp-

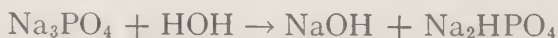
tive and emulsifying properties are more effective in cold than in hot water.

Recently a new type of cleaning agent has been developed which may be named as a sodium alcohol sulphate. The composition of this type of cleaning agent is indicated by the reaction of sulphuric acid with alcohols containing from eight to eighteen or more carbon atoms; the acid thus formed is changed into the sodium salt. The following reactions illustrate the formation of a compound of this type:



Cleaning agents of this kind lower the surface tension of water and emulsify fat as well as or better than soaps. They do not form insoluble compounds in hard water — the calcium and magnesium salts are soluble in water and as effective in cleaning as the sodium salts. Moreover, they are effective in neutral or slightly acid solutions and thus are harmless to protein fibers.

Washing-powders consist of a mixture of soap-powders with sodium carbonate, borax, or sodium phosphate. They serve the purpose of softening the water and of giving an alkaline reaction to aid in cleansing. The alkaline reaction is caused by the formation of sodium hydroxide through hydrolysis of the salts as shown in the typical reaction:



It follows that washing-powders, like alkaline soaps, may have a deteriorating influence upon protein fibers and upon some of the synthetic fibers.

In dry cleaning, the materials are washed in naphtha, a petroleum product that has a lower boiling-point than gasoline. This dissolves the fatty substances and avoids the harmful action of

soap and water on fine protein textiles. The naphtha can be made odorless by removing impurities and can be used repeatedly by filtering under pressure, through a fine powder.

Stain-Removal. — The removal of stain from a fabric is essentially a chemical process. The methods outlined are intended to illustrate the use of chemical reagents and processes in the removal of stains. (A complete list of stains and their removal reagents may be found in texts relating to this subject.) A brief discussion is included also of the effect of these reagents on the fabric and on the dye. In general, the methods for removing stains are of three types: (1) solution of the stain in a suitable solvent, (2) adsorption of the stain by a finely powdered substance, and (3) a chemical reaction which bleaches the stain.

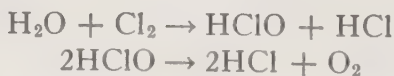
Solvents are used for removing stains when spots of grease or grass-stains (chlorophyll) are dissolved from fabrics. The grease-spots are treated with gasoline or ether as a solvent, and the grass-stains are dissolved by washing with alcohol. Turpentine will remove stains of oil paint; acetone and carbon tetrachloride will dissolve many organic stains. Boiling water will dissolve fresh stains of coffee, tea, or fruit juice. When these stains are allowed to become old or are treated with an alkaline solution, a dark-brown insoluble substance forms that can be removed only by bleaching agents.

Adsorption by fine powders is useful in removing some fresh stains. Flour placed on a fresh ink-stain will adsorb much of the color. French chalk, CaCO_3 , and magnesia, MgO , may be rubbed on grease-spots on heavy textiles to adsorb the grease. If the material is heated to melt the fat, the adsorption takes place more efficiently. Talcum-powder and fuller's earth are other useful adsorbents. These substances are probably less effective than solvents, but they do not have a detrimental action on the fabric.

When a stain resists all solvents and adsorbents, chemical reactions are used to decolorize the stains or to bring them into a soluble form. Many colored stains may be reduced or oxidized to form colorless substances. This chemical reaction is applicable in removing a stain from a white fabric; but colored fabrics may

be decolorized by the reagent. Moreover, a chemical reagent usually weakens the fabric. Before attempting this method of stain-removal, it is well to test the action of the chemical on a sample of the fabric. Sulphur dioxide is used to reduce the yellow color of straw to a colorless compound and to bleach yellow stains. Hydrogen peroxide is another bleaching agent. It decomposes easily to form water and oxygen. Colored materials or stains may be oxidized into a colorless substance by soaking the material in hydrogen peroxide. Potassium permanganate is a more effective oxidizing agent. The use of a deep-purple solution to bleach a color may seem questionable; however, experience has shown us that this compound may be reduced to form a soluble colorless manganous salt. When applied to stains on fabrics, potassium permanganate is reduced to manganese dioxide, a compound in which manganese has a valence of four. A brown color appears as manganese dioxide is precipitated on the fiber. To remove the brown color, the stain is treated with a solution of oxalic acid. This reduces the manganese dioxide to a colorless manganous compound. Many stains that resist all other bleaching agents respond to treatment with this combination.

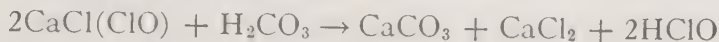
Chlorine gas is one of the most popular and efficient bleaching agents. Its oxidizing action depends on ability to react with water to form hypochlorous acid, which in turn is easily reduced to hydrochloric acid and oxygen. The equations for these reactions are:



In the presence of a reducing agent the oxygen combines with the reducing agent instead of being set free. If the reducing agent is a dye and the oxidized product is colorless, the dye will be bleached by the reaction. If the reducing agent is the protoplasm of some organism, the organism will be destroyed by the reaction. Thus, the solution has both bleaching and disinfectant properties. Most textiles are weakened by long exposure to hypochlorous acid; wool and silk are especially sensitive to its action.

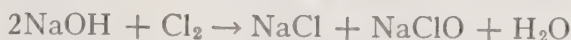
Instead of chlorine gas, hypochlorous acid, obtained from a

salt such as bleaching-powder, may be used. This salt is prepared by passing chlorine gas into lime-water (Chapter XXII). When bleaching-powder is added to a weak acid, hypochlorous acid is formed, as indicated by the reaction

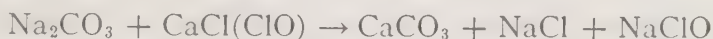


Hypochlorous acid acts as an oxidizing agent, as explained in the previous paragraph. It may oxidize any colored substance with which it comes in contact to a colorless compound.

Chlorine gas may be passed into sodium hydroxide to form sodium hypochlorite. The following equation shows the reaction:

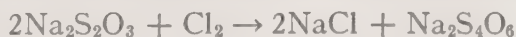


The solution formed by this reaction is known as Javelle water. It is an effective oxidizing agent for use in bleaching or as an antiseptic. Javelle water may be prepared in the home by mixing sodium carbonate solution with bleaching-powder. The equation is as follows:



The insoluble calcium carbonate may be filtered from the mixture, leaving in solution the sodium hypochlorite mixed with sodium chloride. Javelle water is sold under many commercial names for bleaching and antiseptic purposes.

It is important to realize that textile fibers deteriorate when they are boiled with solutions containing bleaching-powder, sodium hypochlorite, or hypochlorous acid. When these bleaching agents are used in dilute solution, the deteriorating effect is less apparent. It is necessary also to rinse the fabric to remove all adhering reagent. After thorough rinsing, the fabric may be soaked in a solution of an anti-chlor to remove the last traces of chlorine. An anti-chlor is a salt which reacts with chlorine to form soluble compounds which are washed from the fabric. Sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$, is a useful anti-chlor. The equation for the reaction of sodium thiosulphate with chlorine is as follows:

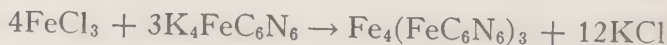


The products of this reaction, sodium chloride and sodium tetrathionate, are removed from the fabric by a final rinsing.

DYEING

The extraction of juice from the indigo plant gives a colorless solution which on exposure to the air forms a blue dye. Indigo is an example of one of the natural dyes. Other important natural dyes are alizarin, obtained from the root of the madder plant; Tyrian purple, obtained from a shellfish; and cochineal, obtained from an insect. It might be said that the extraction of dyes from these sources is not a chemical process. However, chemistry has taken its place in the dye industry; the purification of natural dyes, the preparation of synthetic dyes, and the methods for the application of dyes to fabrics are problems which the research chemist is solving. When we compare the few colors that were available in the natural dyes with the brilliant display of colors that are now shown, it is evident that the chemist has made great progress in the synthesis of dyes. Much has been said about the fastness of dyes; and again we appreciate the work of the chemist as we realize that improved methods for incorporating the dye with the fiber have aided in giving us permanent colors which do not wash out of the fabric or fade in the sunlight. Some of the methods for making dyes and for precipitating them on the fibers will be indicated in this chapter. It would require a separate text to give a complete discussion of the subject.

Mineral Dyes. — The simplest dyes are insoluble colored salts which may be precipitated directly on a fabric; for example, a fabric may be dyed with Prussian blue, $\text{Fe}_4(\text{FeC}_6\text{N}_6)_3$, by dipping the material alternately in solutions of ferric chloride and in potassium ferrocyanide. The equation for this reaction is as follows:



Other colored compounds which may be formed in a similar way are: manganese dioxide, brown; lead chromate, yellow; and iron oxide, tan.

Synthetic Dyes. — With dyes, as with other useful products of nature, the chemist has been curious to know of their composition. The analysis of natural dyes gives a knowledge not only of the elements present in them but of the color-producing groups in the dyes. The analysis indicates too the compounds that may be used in the synthesis of dyes.

It was an important discovery when, in 1856, William Perkin prepared the first synthetic dye from coal-tar. Previously the black, viscous liquid obtained from the destructive distillation of coal was thought to be of little value. Immediately, coal-tar was subjected to rigid investigation and was found to yield many of the compounds needed as foundation materials for the preparation of synthetic dyes. Among the important compounds are: benzene, C_6H_6 ; phenol, C_6H_5OH ; anthracene, $C_{14}H_{10}$; and naphthalene, $C_{10}H_8$. Methods are known by which indigo, alizarin, and Tyrian purple, as well as other natural dyes, may be made synthetically. When made from coal-tar products, indigo is prepared from naphthalene, $C_{10}H_8$, and alizarin is prepared from anthracene, $C_{14}H_{10}$. Tyrian purple is a bromine derivative of indigo. Since the initial preparation of these few synthetic dyes, rapid progress has been made. At the present time there are myriads of dyes made from the products obtained from coal-tar. Synthetic dyes have almost entirely replaced natural dyes.

The Process of Dyeing. — The protein fibers, wool and silk, are dyed more easily and with more permanent colors than the cellulose fibers. There are two explanations that may be offered, both of which have been discussed in Chapter XXXI. Most of the dyes are weak acids or weak bases which can react with the amphoteric protein of the fiber so that the dye becomes a part of the fiber protein. It is a theory, also, that the process may be adsorption. The amphoteric protein (a colloid) possesses a positive charge in acid solution and a negative charge in a basic solution. The weak acids (acid dyes) ionize to give hydrogen ions and colored organic anions. The colored anions may be adsorbed on the positively charged protein (fiber) in acid solution. The weak bases (basic dyes) ionize to form anions and colored organic cat-

ions. The colored cations may be adsorbed on the negatively charged protein (fiber) in a basic solution. In Chapter XXXI these dyes were called acid and basic dyes, respectively. They are more permanent and satisfactory than any other type of dye that can be used on wool and silk.

Cellulose fibers have no amphoteric properties and hence do not respond to acid and basic dyes. Instead of the process just described, a mordant may be used to aid in the incorporation of the dye with the fiber. The mordant acts as an amphoteric colloid and may adsorb either positively or negatively charged dyes. The use of aluminium hydroxide as a mordant in dyeing cellulose fibers is shown in the following procedure. The fabric is soaked in a solution of aluminium sulphate or aluminium acetate until the salt has worked its way into the fibers. The cloth is then dipped into a slightly alkaline solution and steamed. Through these processes, hydrolysis of the aluminium salt occurs. This is shown by the equation



Aluminium hydroxide is precipitated all through the fabric, not only on the surface but within the separate fibers. When the material is dyed, the aluminium hydroxide adsorbs the dye, forming a fast color. Several compounds may be used as mordants: for example, stannous salts, iron salts, chromium salts, and tannic acid. The action of the mordant is specific; that is, with certain dyes, some mordants give better results than others.

Cellulose fibers may be dyed by a process in which the dye is precipitated throughout the material. Just as ferric ferrocyanide may be precipitated on cotton by permeating it first with ferric chloride and then with potassium ferrocyanide, so complex organic compounds such as indigo may be precipitated directly on a fiber. Reduced indigo is a soluble yellow dye which may be permeated throughout the cotton fiber; when the fiber is exposed to the air, the yellow compound is oxidized to an insoluble blue dye, precipitated through the fibers in such a way that it cannot bleed or dissolve in water.

There are methods for the application of dyes to the fibers

that are not included in this brief summary. Because many dyes are of a colloidal nature, the processes for precipitation of colloids are applicable to some methods of dyeing. One of these precipitation methods is illustrated in the use of a salt, such as sodium sulphate, in the dye bath. The influence of the electrolyte in neutralizing the charge upon a colloid (the dye), and hence in precipitating the colloid, has been described in Chapter XXXI. The electrolyte, then, aids in precipitating the dye within the fibers of the textile.

The wide variety of dyes available cannot be described in terms of the brief classification just given. There are dyes that are adaptable for cotton, and other dyes that are fast on silk and wool; the properties of the fibers as well as of the dyes must be considered in all dyeing processes. Synthetic fibers do not adsorb the dyes used for other fibers. These fibers are not amphoteric and so cannot react chemically with acid and basic dyes. The fibers are smooth; thus there is no rough surface to aid in the adsorption of the dye. New dyes have been prepared, however, which combine with the synthetic fibers to give satisfactory results. When mixtures of fibers are dyed, the cloth may be treated successively with dyes that react with one of the fibers only. Thus two-color effects may be obtained in the textile at less cost than by weaving fibers of different colors.

QUESTIONS AND PROBLEMS

1. Give the source of the four types of natural fibers. Tabulate their microscopic appearance, method of burning, action with acid, action with alkali, heat conductivity, property of absorbing moisture.
2. What properties are used to distinguish cotton from wool, rayon from silk, and linen from cotton?
3. What is mercerized fiber, celanese, nylon, weighted silk?
4. What are the four types of rayon? Compare their properties.
5. Give three ways in which soaps for cottons differ from soaps for silks.
6. Which of the three general methods of stain removal apply in the following:
 - (1) dye removed with hydrogen peroxide
 - (2) rust removed with lemon juice and salt
 - (3) grape juice removed with hot water

- (4) grease removed with soap solution
 - (5) paint removed with turpentine
 - (6) old coffee stains removed with Javelle water
 - (7) grass stains removed with chloroform
 - (8) India ink removed with lard.
7. Why is oxalic acid used after potassium permanganate on a stain? Why is sodium thiosulfate used after a chlorine bleaching agent?
 8. Give the equation for the preparation of Javelle water from bleaching-powder. Give two uses of Javelle water in the home.
 9. Give four examples of mineral dyes. Why are they fast colors?
 10. What are synthetic dyes? From what are they made? How do they compare with natural dyes? Give two examples of natural dyes.
 11. Explain the action of basic dyes. On what materials are they used?
 12. Explain the action of a mordant. On what materials are mordants used?
 13. Why is salt added to a dye bath?

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CHAPTER XXXV

THE SILICATE INDUSTRIES

SILICON is the second element in abundance in the earth's crust. Like other active elements, it is found in nature only in combination, and it is difficult to obtain silicon in the free state. Rocks, sand, clay, and all soils are made up principally of silicon compounds. Silicon is placed just below carbon in the periodic table, and its compounds are as important in minerals as carbon compounds are in organic matter. The chemistry of silicon is probably as complex as that of carbon but is not so closely related to our daily life; hence it has been studied less extensively. When silicon compounds are used in making glass, cement, or pottery, the chemical changes are important and it is desirable to understand them fully.

Silicon dioxide, SiO_2 , known as silica, occurs in a variety of familiar forms. Amethysts and quartz are examples of crystalline silica. Certain organisms in the sea have skeletons of silicon compounds instead of calcium compounds. These skeletons accumulate in the bottom of the sea as finely divided silica, called diatomaceous or infusorial earth. It is used as a scouring-powder. Silica is found in the ash of all plants and of some animal tissues.

When silica is heated in the electric furnace, it becomes soft at about $1,200^\circ \text{C}$. and melts to a viscous liquid at approximately $1,600^\circ \text{C}$. At this temperature it may be worked like glass and molded into different shapes. Air, dispersed through melted quartz, makes the glass opaque and rough. Recently it has been shown that by fusing quartz in a vacuum and compressing it, these air bubbles can be removed, giving a clear, transparent glass. This fused silica, called quartz glass, is ideal for window-glass because it transmits the health-giving ultraviolet rays as well as other light-rays. However, the preparation of this glass is so difficult and expensive that it is not in common use. Quartz glass

is a highly desirable material for baking dishes and for laboratory utensils because it has a small coefficient of expansion and so withstands sudden changes in temperature. Its use in apparatus is effective because it is resistant to corrosion by most chemicals. A fine grade of quartz glass is coming into use for lenses and for ultraviolet tubes and similar apparatus. Our hope is that research workers will develop less expensive methods for the preparation of this valuable glass and thus make possible its more general use.

The oxide of aluminium is closely associated with silica in certain compounds. This oxide, Al_2O_3 , called alumina, occurs in nature as corundum, emery, and sapphires. Many other gems are composed of mixtures of aluminium oxide with silica, probably as aluminium silicate. Aluminium oxide melts at about $1,900^\circ \text{C}$. It has been shown that it is possible to prepare from it a variety of artificial gems. Alumina can be melted in an oxyhydrogen flame, and by slow feeding of the powdered alumina to a small crystal acting as a nucleus in the hot flame large crystals may be formed. If pure alumina is used, white sapphires can be made. If traces of colored metallic oxides are added, sapphires of every color are formed. Chromic oxide in varying amounts forms every shade of ruby desired. These crystals are identical in composition with the natural gems and can be made free from blemishes.

Silicon, in Group IV of the periodic table, forms the two acids, orthosilicic acid, H_4SiO_4 , and metasilicic acid, H_2SiO_3 . Salts of both of these acids are known as well as of several other silicic acids, such as $\text{H}_6\text{Si}_2\text{O}_7$, $\text{H}_8\text{Si}_3\text{O}_{10}$, and $\text{H}_4\text{Si}_3\text{O}_8$. The simplest and best known of the salts of silicon is sodium metasilicate, Na_2SiO_3 . Although this formula is similar to that for sodium carbonate, the physical properties of the salt are quite different. Sodium silicate is most familiar as a colloidal, jelly-like sol, commonly called water-glass. In this form, it has a variety of uses, e.g., in the preservation of eggs, as a constituent of soaps and washing-powders, and as a cement or mineral glue.

When any acid is added to a sodium silicate solution, a more solid gel of metasilicic acid separates. This is shown by the equation



By dialyzing this gel in a collodion sac, the salts can be removed, and a colloidal gel of silicic acid is obtained. As water evaporates from this gel, the acid will decompose, forming the anhydride, SiO_2 , as a white, porous gel. This silica gel is valuable as an adsorbent, replacing charcoal in some industries. Opals are a form of colloidal silica containing from 1 to 12 per cent of colloiddally dispersed water. Agates and flint, micro-crystalline forms of silica, were probably formed in nature by dehydration of silica gel accompanied by pressure. They are as hard as quartz.

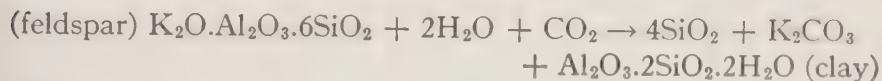
Many crystalline minerals have been analyzed and identified as salts of different silicic acids. A number of forms are familiar; for example, asbestos is usually given the formula $\text{CaSiO}_3 \cdot 3\text{MgSiO}_3$; garnet is found to be $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$; certain kaolins or china clays have the formula $\text{H}_2\text{Al}_2(\text{SiO}_4)_2 \cdot \text{H}_2\text{O}$; and one type of feldspar has the formula KAlSi_3O_8 . On the other hand, since most minerals have not been synthesized in the laboratory, it cannot be said that these formulas have been definitely proved. It is probably more nearly accurate to write the formulas, as is usually done in industry, as oxides of the elements without indicating the method of combination. As an example, the type of feldspar just given may be written $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$, and the formula of the china clay may be written $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. This gives the proportion of each element present as determined by analysis, which in many cases is all that is definitely known.

The analysis of these minerals is made more difficult because analyses of different samples of minerals similar in properties indicate different compositions. Most feldspars contain both sodium and potassium, and iron may replace some of the aluminum in other samples. There is such abundant opportunity in nature for the mixing of substances that the crystallization of a pure salt of constant composition is almost impossible. In all industries a knowledge of the composition and formulas of the materials used and of the nature of the chemical changes that take place is important in manufacturing standard products and in devising new products. In the silicate industries to-day, all materials are analyzed and the proportion of each compound used is kept within definite limits. Research chemists are studying

continually the chemical changes that take place and the compounds that are formed when pure oxides of two or more elements are heated together. They are attempting to devise different mixtures of materials or better methods of treating them to prepare more satisfactory products.

When mineral silicates are heated, they melt to a viscous liquid which, instead of crystallizing to a solid when cooled, slowly forms an amorphous substance. This property makes it impossible to obtain these salts in the pure crystalline form that is necessary for the determination of their structure. It is this glass-forming property, however, that makes the silicates important in industry.

The clays are colloidal hydrated aluminium silicates, formed from the decomposition of the feldspars by the action of water and air. An equation illustrates the reaction:

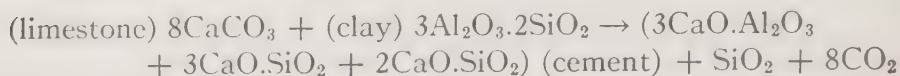


Other minerals are usually mixed with the clays. For the finer porcelains these are removed by suspending the clay in a slow-moving stream of water. The sand and larger particles settle quickly, but the colloidal clay particles are carried with the stream to a settling tank, where the water is evaporated and the clay dried. When mixed with water, clay becomes plastic and may be molded. Like other silicates, it has no definite melting-point, but when heated it loses its moisture. At approximately 900° C. the more fusible components soften, cementing together the rest of the mixture.

Mortar and Cement. — Mortar is a mixture of calcium hydroxide and sand with water. When it is mixed into a paste and allowed to stand, some of the water evaporates and the remainder is held as a gel by the formation of hydrated calcium hydroxide crystals. This gel formation brings about the first hardening of the mortar. If the gel is exposed to the air, the slaked lime on the surface reacts with the carbon dioxide of the air to form calcium carbonate, as shown in the equation

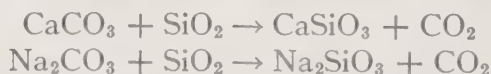


Portland cement was discovered in a search for a mortar that would harden under water. It is made by mixing and heating limestone with clay in definite proportions. The reactions that take place may be represented as follows:



The calcium aluminate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, formed by this reaction, hydrates in a few hours under water. Usually, in twenty-four hours the silicate, $3\text{CaO} \cdot \text{SiO}_2$, hydrates, forming a stiffer gel or a harder cement. After several months the compound $2\text{CaO} \cdot \text{SiO}_2$ slowly begins to hydrate. By changing the proportions of these three compounds and by adding other oxides, the properties of cements may be varied.

Glass. — Most types of glass consist of a mixture of silicates melted together and cooled to a solid without crystallizing. Glass has no definite melting-point and therefore must be considered as an amorphous solid or an undercooled liquid. Ordinary lime-soda glass used for window-panes and bottles is made by heating sand, SiO_2 , limestone, CaCO_3 , and sodium carbonate, Na_2CO_3 , or sodium sulphate, Na_2SO_4 , to a temperature of $1,260^\circ \text{C}$. The proportion of these ingredients must be kept within definite limits to obtain a satisfactory glass. The limestone and soda react with the sand to form silicates and carbon dioxide as in the equations:



The principal compound formed is a mixed salt with the composition $\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 6\text{SiO}_2$.

Plate-glass has the same composition as ordinary window-glass, but it is made from carefully selected materials. The clear, viscous glass is poured on a steel table and flattened with a steel roller into a sheet. It is then polished with rouge (iron oxide). The common bottle-glass may have a green or yellow color from iron compounds present as impurities in sand. To prevent this color in the better types of glass, manganese dioxide is added to

oxidize the iron compounds. The manganese also gives a pink color to neutralize the color of the ferric impurities.

Glasses with different properties are made by substitution of other elements in varying proportions for calcium or sodium. Aluminium oxide in small proportions makes a glass that is resistant to heat changes and also a product that is easily molded and worked. Substituting lead for calcium compounds and potassium for sodium compounds makes a hard glass which is used for optical lenses and for cut glass. Small quantities of the oxides of boron, barium, zinc, aluminium, and arsenic or other elements are often added to give glass more desirable properties. Pyrex glass is used extensively for laboratory utensils and kitchen ware because it has a low coefficient of expansion, making it unusually resistant to rapid changes in temperature; Pyrex glass is desirable also because it is not easily attacked by chemicals or broken by mechanical action. It is composed of a high proportion of silica (80 per cent) with boron oxide and about 4 per cent of sodium oxide. Recently a glass has been developed from which all of the constituents except silica and 3.6 per cent of boron oxide are dissolved in acid after the utensils have been molded from it. In this way, a glass is made that contains over 96 per cent silica and that has many of the properties of silica glass but is less expensive; it has a high resistance to heat, chemical and mechanical action, and transmits ultraviolet light.

Color is given to glass by dissolving colored mineral salts or oxides in the melted glass. In a few cases as in ruby glass, the red color is obtained by a colloidal dispersion of a metal (gold) throughout the glass. By varying the composition of the glass and the rate of cooling as well as the coloring agents, almost any desired color may be obtained in glass.

Industry is constantly developing new glasses suitable for a wide variety of uses. For automobile windows, a safety glass is made by using a layer of tough transparent plastic between two thin layers of glass like a sandwich; by using Polaroid material for the plastic film, a glass is made that eliminates glare. Fine glass fibers, 0.0004 inch in diameter, that can be woven into cloth are made by forcing the molten glass through fine holes into

a jet of steam. Glass fibers in the form of either glass wool or a new sponge-like glass filled with air bubbles are used for insulation in houses.

In order to prevent contamination of the contents, the bottles used for serums and drugs are made from a glass that is unusually resistant to chemical action. The new fluorescent lamps (Chapter XXX) require glasses that are resistant to vapors and that transmit or absorb certain colors. The glass insulators on electric lines must be resistant to electricity. Plate glasses have been made heavy enough to use as wainscoting or walls in buildings. The use of automatic machines to mold bottles, light bulbs, and other objects used in abundance, make these objects much less expensive, but the machines require a glass that is constant in composition and properties.

Enamels. — Enameled metal is made by coating iron or steel with a hard glass to give a material with the strength of iron and the properties of glass; in other words, an unbreakable glass. Enamels are more difficult to prepare than glasses. Besides having a pleasing appearance and a resistance to the action of weak acids and alkalies, enamels must be made to adhere to the metal without cracking or peeling and must have the same coefficient of expansion as the metal to prevent cracking when subjected to sudden changes in temperature. Since the inclusion of lead oxide in a glass makes it harder and more resistant to chemical action, this compound is generally used in making the glass for enamels. Lead compounds are poisonous, which means that there is danger of poisoning when the enamel of cooking utensils chips off and gets into the food. For this reason we are cautioned not to use enamel-ware after the enamel has begun to crack, and not to allow food to stand in enameled dishes for a long time.

Pottery. — Pottery is often defined so as to include all articles made of clay. It is usually classified into two types: (1) porous pottery, including bricks, tiles, and refractory ware, and (2) non-porous pottery, including earthenware and porcelain. The natural composition of many clays is such that, when water is added,

the clay can be molded into a product which will dehydrate on heating. At a higher temperature the constituents will be cemented together by the fused materials. This vitrifying process may be continued until the pottery is non-porous and impermeable to water.

Bricks made of ordinary clay will melt and lose their shape if heated above $1,000^{\circ}\text{C}$. Some clays, however, do not melt until heated above $1,600^{\circ}\text{C}$. Bricks made of such clay are invaluable for kilns in which to fire porcelain, and for the crucibles used in melting glass and steel. Pottery may be made non-porous by coating it with a glaze or glass. Coarse earthenware is made from a single clay with little care given to the impurities that may be present. In the finer English earthenware, a purer china clay is used and mixed with feldspar and flint or quartz. When this ware is fired, the feldspar fuses at a lower temperature than the clay and cements it into a hard, durable earthenware. The glaze is then added to make it non-porous. If the glaze is cracked or chipped off, the ware becomes permeable at that point and turns dark from the grease and dirt absorbed.

Glazing of earthenware is sometimes accomplished by throwing salt on the pottery when it is ready to remove from the kiln. The salt melts and combines with the silicates of the clay, forming a glassy surface or glaze impermeable to water. Better glazes are applied to earthenware by dipping the articles into a thin paste containing materials similar to those used in the body of the ware, which on firing forms a glassy surface. The composition of the glaze paste must be carefully controlled. Slight variations may make a glass that cracks on cooling or peels off the earthenware. As in enamels, the most successful glazes contain lead compounds.

The materials used for fine porcelain are the same as in the better types of earthenware, except that they are more carefully selected. The articles are fired until the component materials are not only cemented together but so vitrified throughout that they are impervious to moisture. The glazes are made of the same ingredients as the body with a larger proportion of calcium carbonate to make it fuse more readily. Since the body as well

as the glaze is vitrified, porcelain does not become permeable to water and grease when the glaze is chipped off. In the best porcelain, the gradual transition of properties between the glaze and the vitrified body gives a soft, translucent appearance that is often more pleasing than either glass or semi-porcelain.

QUESTIONS AND PROBLEMS

1. Compare the uses and properties of silicon dioxide and aluminium oxide.
2. Give formulas for three acids of silicon.
3. Give three uses of water-glass. Explain its action in each case.
4. Explain the chemical nature of flint, pearls, opals, agates, asbestos, feldspar, mortar, cement, glass, Pyrex glass, enamel, quartz glass, glaze on pottery, sand, emery, slaked lime, diamond.
5. Compare the process of manufacture of bricks, porcelain, and semi-porcelain.

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SUPPLEMENTARY STUDY QUESTIONS

Chapters I to IV

1. A box measures 8 cm. \times 6 dm. \times 2 dm. (a) Express the dimensions in inches and in meters. (b) What is the volume of the box in cubic centimeters? in liters? Express the volume in quarts. (c) Find the weight of water at 3.8° C., that the box would contain. (d) Calculate the weight of air and of butter-fat contained in the box (1 liter of air weighs 1.3 g.; 1 c.c. of butter-fat weighs 0.9 g.).
2. How many liters in a gallon? What is the weight of a gallon of chlorine gas? (1 liter of chlorine gas weighs 3.17 g.).
3. Distinguish between the terms: compound and mixture; physical change and chemical change; law and theory; molecules and atoms; synthesis and analysis. Distinguish between the units: liter and quart; meter and yard; gram and cubic centimeter; millimeter and kilometer.
4. The formula for ammonia gas is NH_3 . (a) Is it an element or a compound? Explain your answer. (b) How many atoms of each element in the molecule? (c) Show by an equation, how ammonia is made from hydrogen and nitrogen.
5. (a) Write four equations to show different methods for the preparation of oxygen. Which reaction is used for the laboratory method? Explain why electrolysis of water could be used commercially. (b) Write four combination reactions of oxygen with other elements. (c) Write the combination reaction of iron with sulphur. (d) Write an equation to show the decomposition of sugar.
6. The following equation is balanced:



- (a) Name and state the number of molecules of each substance entering into the reaction; in the product. (b) How many atoms of each element enter into the reaction? How many atoms of each element are in the product? (c) Why is the equation said to be "balanced"?
7. Give the physical and chemical properties which characterize the following, and tell how the substances have been used in the laboratory: potassium chlorate, magnesium, manganese dioxide, sugar, mercuric oxide, sulphur.
8. When 45 c.c. of hydrogen and 45 c.c. of oxygen are mixed and ignited, keeping the gases above 100° C., what volume of steam is formed?

What gas will be left over after combination occurs, and what volume of gas?

9. When 6 liters of hydrogen and 5 liters of oxygen are mixed and ignited, keeping the gases above 100°C ., how many liters of steam will be formed? What gas will be left over and what volume of the gas?
10. When 6 grams of hydrogen and 24 grams of oxygen are mixed and ignited, are the gases in the correct weight proportion for all to be used? If not, tell which gas is not all used, and how many grams of it is left over? What weight of water is formed?
11. What weight of hydrogen will combine with 12 grams of oxygen? What weight of water will be formed?
12. Diagram and explain: the calorimeter, the apparatus for electrolysis of water, the laboratory method for the preparation of oxygen.
13. A sample containing 1.8 grams of food is burned in a calorimeter. The temperature of 1,500 grams of water is raised from 22°C . to 28°C . Calculate the calorific value per gram of food.
14. Tell how a supersaturated solution is made.
15. Tell two important ways in which a solution differs from other mixtures.
16. Distinguish between the terms: solute and solvent; supersaturated and unsaturated solutions.
17. List three factors that affect the rate of a chemical reaction. What is a catalyst?

Chapters V to VII

1. The formula for freon, a refrigerator gas, is CCl_2F_2 . (a) How many atoms of each element in the molecule of the compound? (b) What is the gram-molecular weight of the compound? (c) Calculate the percentage composition.
2. Answer the questions as in 1 (a, b, c) for carbon dioxide, CO_2 ; for phosphorus pentoxide, P_2O_5 ; for chlorine, Cl_2 .
3. Calculate the simplest formulas for the three compounds of the following percentage composition:
 - (1) 59.57 per cent iron and 40.43 per cent fluorine
 - (2) 6.62 per cent aluminium and 93.38 per cent iodine
 - (3) 52.2 per cent carbon, 13 per cent hydrogen, and 34.8 per cent oxygen.
4. Calculate the weight represented by the expression: 3Cl_2 . It is the weight of how many molecules of chlorine?
5. Two hundred and forty-four grams is the weight of how many molecules of potassium chlorate?
6. How many grams of iron will be formed by the reduction of 80 grams of ferric oxide with carbon?
7. How many grams of aluminium will react with 150 grams of hydrochloric acid?

8. How many grams of potassium chloride will be obtained by heating four grams of potassium chlorate?
9. Compare the terms: exothermic and endothermic reactions; combination and decomposition reactions; oxidation and reduction reactions; gram-molecular weight and gram-atomic weight; ion and atom; neutron and electron.
10. Make diagrams and explain the structure of the atoms of lithium, hydrogen, and chlorine. Explain fully how the structure of these atoms determines their characteristic valence.
11. From the number of electrons in the outer orbit of the atoms of each of the following elements, determine the valence of the element:

bromine 7 electrons

barium 2 electrons

aluminium 3 electrons

sulphur 6 electrons

carbon 4 electrons

phosphorus 5 electrons

12. From the valence, determine the number of electrons in the outer orbit of the atoms of each of the following elements: chlorine, nitrogen, sodium, oxygen, zinc.
13. Write formulas for the compounds:

silver oxide

ammonium chloride

copper iodide

magnesium nitride

ferric hydroxide

calcium sulphate

potassium sulphide

sodium oxide

zinc chloride

mercuric sulphate

ferrous sulphide

sodium chlorate

barium chlorate

zinc hydroxide

potassium hydroxide

silver sulphate

ammonium sulphate

aluminium sulphate

14. Complete and balance the following equations:

1. barium hydroxide + sodium sulphate

2. zinc sulphate + potassium sulphide

3. ammonium hydroxide + ferric chloride

4. ferric oxide + hydrochloric acid

5. copper iodide + potassium hydroxide

6. ammonium sulphate + sodium hydroxide

7. aluminium chloride + sulphuric acid

Chapters VIII and IX

1. Explain the terms: Absolute thermometer scale, pressure of gas expressed in mm. of mercury, aqueous vapor tension, standard temperature and pressure, boiling-point, freezing-point, heat of condensation, heat of fusion.
2. Express the volume-temperature (Charles') law and the volume-

pressure (Boyle's) law in your own words. How are these laws explained by the molecular theory?

3. A volume of dry gas measures 700 c.c. at 27° C. and 750 mm. pressure. What is the volume of gas at standard conditions?
4. A quantity of gas measured over water occupies 1,050 c.c. at 24° C. and 738 mm. pressure. What is the volume at standard conditions?
5. At standard conditions, the weight of 400 c.c. of carbon dioxide gas is 0.786 gram. Calculate the gram-molecular weight and the weight of one liter of the gas.
6. From the formulas, calculate the weight of 800 c.c. of chlorine; 600 c.c. of ammonia; 12 liters of nitrogen; 8 liters of sulphur dioxide.
7. Find the gram-molecular weight of a gas, when 690 c.c. of it, at standard conditions, weighs 0.99 gram.
8. Using the following results of a laboratory experiment, determine the gram-molecular weight of oxygen and the per cent of oxygen in potassium chlorate:

Weight of potassium chlorate.....	3.26 g.
Weight of residue (potassium chloride)....	1.98 g.
Volume of oxygen (over water).....	1,022 c.c.
Temperature.....	22° C.
Pressure.....	740 mm.
Aqueous vapor pressure.....	19.8 mm.

Compare the results with the gram-molecular weight of oxygen obtained from a formula, and with the per cent of oxygen in potassium chlorate as determined from the formula.

9. A liter measuring cylinder (or a quart glass jar) is inverted over water in a room in which the temperature is 30° C. and the pressure is 740 mm. What is the nature of the volume change in the gas if the temperature is lowered; if the temperature rises; if the air pressure becomes less; if the air pressure becomes greater? Calculate the weight of air in the liter bottle and in the quart bottle at standard conditions (1 liter of air at standard conditions weighs 1.29 grams).
10. A quantity of carbon dioxide gas, collected over water, measures 1,318 c.c. at 737 mm. pressure and 27° C. The gas weighs 2.2 grams. Use the data to calculate the weight of one liter of carbon dioxide gas at standard conditions; determine the gram-molecular weight of carbon dioxide. Compare the calculated value with the gram-molecular weight of carbon dioxide obtained from a formula. The gas contains 27.27 per cent of carbon; what is the weight of carbon in the gram-molecular weight of carbon dioxide?
11. Explain the principles involved in the use of the barometer; the thermometer; the pressure cooker; the refrigerating unit. Explain the process of distillation of water.

12. When 15 grams of potassium chlorate are heated, how many liters of oxygen gas will be obtained? This volume of oxygen (at standard conditions) will occupy how many liters at 20° C. and 742 mm. pressure?
13. When 30 grams of zinc react with sulphuric acid, how many liters of hydrogen gas will be formed? This volume of hydrogen (at standard conditions) will occupy how many liters at 15° C. and 730 mm. pressure?
14. Ferric oxide reacts with 200 liters of hydrogen gas, measured at 18° C. and 725 mm. pressure. What weight of iron is formed?
15. A quantity of chlorine gas measuring 400 c.c. at 22° C. and 730 mm. pressure will react with how many grams of copper?
16. What weight of copper will be formed when 1.2 grams of copper oxide is reduced with hydrogen gas?

Chapters X to XII

1. Write formulas for the following compounds. Classify each as acid, base, or salt; if a salt, designate as an acid, basic, or mixed salt.

potassium hydrogen carbonate	potassium hydroxide
sodium sulphite	sodium hydrogen oxalate
hydrogen sulphate	ammonium nitrite
calcium hydroxy chloride	barium phosphite
potassium phosphate	calcium chlorite
ammonium sulphate	sodium ammonium hydrogen phosphate
ammonium hydroxide	hydrogen sulphide
calcium acetate	ammonium carbonate
barium chlorate	aluminium chloride

2. Complete and balance the following reactions:
 - aluminium hydroxide with sulphuric acid
 - ferrous nitrate with ammonium sulphide
 - calcium hydroxide with phosphoric acid
 - barium nitrite with potassium sulphate
 - sodium hydroxide with magnesium chloride
 - potassium oxide with hydrochloric acid
 - ammonium phosphate with ferric hydroxide
 - silver nitrate with zinc chloride
3. Write six neutralization equations. In each designate which compound is an acid, a base, and a salt.
4. Write formulas for three hydrates, four acids, four bases, two acid salts, and two basic salts.
5. Write equations to illustrate the preparation of nitric acid from its acid anhydride; of sulphuric acid from its acid anhydride. Use graphic formulas also, to show each equation.

6. Write equations to illustrate the preparation of magnesium hydroxide from its basic anhydride; of sodium hydroxide from its basic anhydride; of calcium hydroxide from its basic anhydride. Use graphic formulas also, to show each equation.
7. How many grams of acetic acid are present in three liters of one-molar solution; in 300 c.c. of six-molar solution; in four liters of tenth-molar solution?
8. How many grams of sulphuric acid are present in two liters of one normal (1N) solution; in seven liters of 2N solution; in 200 c.c. of 0.5N solution?
9. Calculate the molarity and the normality of a solution that contains 39.2 g. of sulphuric acid in 500 c.c.; of a solution that contains 13.5 g. of sulphuric acid in three liters of solution; of a solution that contains 15 g. of acetic acid in 250 c.c. of solution.
10. In a titration experiment, 36 c.c. of 0.4N solution of sodium hydroxide neutralized 48 c.c. of a solution of sulphuric acid. Calculate the normality of the sulphuric acid solution. How many grams of acid in each liter of sulphuric acid solution?
11. How many c.c. of 0.2N hydrochloric acid will neutralize 60 c.c. of 0.7N solution of sodium hydroxide?
12. Write molecular formulas and graphic formulas for: sodium chloride, magnesium chloride, aluminium chloride, sodium oxide, magnesium oxide, aluminium oxide, sodium nitride, magnesium nitride, aluminium nitride.
13. Explain the use of the X-ray diffraction patterns to determine the kind of compounds that are electrovalent and the kind of compounds that have covalent bonds.
14. By using valence electrons, diagram the following compounds to show whether each is electrovalent or covalent: NaCl, CaCl₂, CO₂, NH₃, Cl₂.
15. Explain the terms: anhydrous salt, anhydride, efflorescent, deliquescent, indicator, neutralization, gram-equivalent weight, molar solution, normal solution, non-polar compound, coördinate valence, electrolyte.

Chapters XIII to XVI

1. A solution containing one gram-molecular weight of magnesium chloride (assume complete ionization) dissolved in a liter of water, contains how many ions? Calculate the boiling-point of the solution.
2. A solution containing one tenth of a gram-molecular weight of aluminium sulphate (assume complete ionization) dissolved in a liter of water, contains how many ions? Calculate the freezing-point of the solution.

3. What is the gram-molecular weight of a non-electrolyte of which 37.9 g. in 1,000 g. of water boils at $100.34^{\circ}\text{C}.$?
4. What is the concentration in g. per 1,000 c.c., of a sugar ($\text{C}_6\text{H}_{12}\text{O}_6$) solution that has a freezing-point of $0.66^{\circ}\text{C}.$?
5. How many liters would hold 176 grams of carbon dioxide gas at standard temperature and pressure?
6. How many grams of calcium carbonate would be dissolved in 27 c.c. of 0.25N hydrochloric acid?
7. Write equations to show the hydrolysis of the following salts: ferric chloride, zinc carbonate, potassium phosphate, ammonium sulphide, sodium carbonate. Why is there no hydrolysis in a solution of sodium chloride?
8. Write five displacement reactions using acetic acid with metals that will react; write each equation to show the ionic changes.
9. Write five double decomposition reactions in which a precipitate forms; write each equation to show the ions that interact to form the precipitate.
10. Write five double decomposition reactions in which a gas is formed; write each equation to show the ions that interact to form the gas.
11. Write five neutralization equations; tell why they go to completion.
12. The following reactions include displacement, double decomposition, and hydrolysis reactions; complete each equation and classify. For displacement or a double decomposition reaction, rewrite to show the interaction of the ions:
 - magnesium with zinc nitrate
 - potassium carbonate with water
 - ferrous carbonate with oxalic acid
 - copper with mercuric chloride
 - potassium chloride with sulphuric acid
 - aluminium with copper chloride
 - acetic acid with ammonium hydroxide
 - copper sulphate with water
 - aluminium chloride with silver nitrate
 - mercuric chloride with iron
13. Write equations to show three methods for the preparation of calcium oxide.
14. Write equations to show five methods for the preparation of magnesium chloride.
15. Write equations to show methods for the preparation of the following:
 - zinc chloride from zinc carbonate
 - magnesium oxide from magnesium carbonate
 - aluminium sulphate from aluminium
 - ferrous sulphate from ferrous hydroxide

ammonium sulphide from ammonium hydroxide
aluminium chloride from aluminium sulphate
potassium nitrate from potassium chloride
potassium sulphate from potassium chloride

16. Explain the terms: hydrolysis, precipitate, reversible reaction, mass law, hydrogen ion concentration, pH value, buffer mixture, destructive distillation, allotropic forms of an element, hydronium ion, strong electrolyte, electroplating, electrolysis.
17. Give the formulas for: marble, baking-soda, diamond, dry-ice, lime-water.
18. Give the commercial uses of the following: carbon dioxide, carbon monoxide, the allotropic forms of carbon.
19. How many grams of calcium carbonate would be precipitated by the reaction of eight liters of carbon dioxide with lime-water?

Chapters XVII-XX

1. Balance the following oxidation-reduction reactions:
 - (1) $I_2 + HNO_3 \rightarrow NO_2 + H_2O + HIO_3$
 - (2) $K_2Cr_2O_7 + H_2S + H_2SO_4 \rightarrow S + KHSO_4 + Cr_2(SO_4)_3 + H_2O$
 - (3) $K_2Cr_2O_7 + KI + HCl \rightarrow KCl + CrCl_3 + I_2 + H_2O$
 - (4) $Sb + HNO_3 \rightarrow H_2O + NO + Sb_2O_3$
 - (5) $SnCl_2 + HIO_3 + HCl \rightarrow SnCl_4 + HI + H_2O$
 - (6) $PbS + HNO_3 \rightarrow PbSO_4 + NO + H_2O$
 - (7) $KBrO_3 + KI + HCl \rightarrow KCl + KBr + I_2 + H_2O$
 - (8) $KMnO_4 + H_2S + H_2SO_4 \rightarrow KHSO_4 + MnSO_4 + S + H_2O$
 - (9) $S + HBrO_3 + H_2O \rightarrow H_2SO_4 + Br_2$
 - (10) $HNO_2 + HBrO_3 \rightarrow HNO_3 + Br_2 + H_2O$
2. Write equations to show the laboratory method for the preparation of: nitrogen, nitric acid, ammonia, sulphur dioxide, hydrogen sulphide. Diagram the apparatus used in the preparation of each substance. Describe the physical and chemical properties of each substance.
3. Describe a commercial method for the preparation of: ammonia, nitric acid, nitrogen, sulphur, sulphuric acid.
4. Describe the physiological effect of breathing: oxygen, nitrogen, sulphur dioxide, hydrogen sulphide, nitrous oxide, carbon dioxide, carbon monoxide.
5. Write equations for the following reactions; tell what is to be observed when each occurs:
 - (1) copper with concentrated nitric acid
 - (2) copper with concentrated sulphuric acid
 - (3) zinc with dilute sulphuric acid
 - (4) ferrous sulphide with hydrochloric acid

- (5) copper oxide with hydrochloric acid
 - (6) sodium hydroxide with ammonium chloride
 - (7) barium chloride with zinc sulphate
 - (8) hydrosulphuric acid with lead acetate
 - (9) ammonium sulphide with silver nitrate
 - (10) sodium sulphite with hydrochloric acid
6. Give the formulas and commercial uses of sulphur dioxide, sulphuric acid, ammonia, calcium cyanamide, brimstone, Chile saltpeter, nitrous oxide, blue vitriol.
 7. Explain and illustrate the terms: nitrogen fixation, desiccator, Frasch process for mining sulphur, oxidizing agent, reducing agent, air-conditioning, absolute humidity, relative humidity, ozone.
 8. What are the commercial uses of helium, neon, and argon?
 9. What is the formula, name, and color of the insoluble compound formed in the test for hydrogen sulphide gas? Write the ionic equation to form the compound.
 10. What is the formula, name, and color of the insoluble compound formed in the test for sulphate ion? Write the ionic equation to form the compound.
 11. What is the formula and physical properties of the gas formed in the test for ammonium ion? Write the ionic equation to show the formation of the gas.
 12. Write equations to show the oxidation-reduction reactions of nitric acid with hydrogen sulphide, forming (a) sulphur as a product, and (b) sulphuric acid as a product. For each reaction, indicate the change in valence.
 13. Balance the following oxidation-reduction reactions; indicate the oxidizing agent and the reducing agent in each:
 - (1) $\text{Hg} + \text{HNO}_3 \rightarrow \text{Hg}(\text{NO}_3)_2 + \text{NO}_2 + ?$
 - (2) $\text{PbS} + \text{HNO}_3 + \text{HCl} \rightarrow \text{PbCl}_2 + \text{S} + \text{NO} + ?$
 - (3) $\text{Al} + \text{H}_2\text{SO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3 + \text{SO}_2 + ?$
 - (4) $\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2\text{S} + ?$
 - (5) $\text{Zn} + \text{HNO}_3 \rightarrow \text{Zn}(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3 + ?$

Chapters XXI to XXIII

1. What valences have all elements in Group VII of the periodic table? Use diagrams and an explanation to show why fluorine and chlorine have the same valence. Which is the stronger acid-forming element?
2. Arrange the following elements in the order of the strongest base-forming to the strongest acid-forming: Cl, S, As, Rb, Ge, Br, Ga, Zn.
3. Using the phosphorus family of Group V as an illustration, show how the properties of the elements change with increasing atomic weight.

4. Write formulas for: hydrogen sulphide, sulphur trioxide, sulphuric acid; write formulas and names of the corresponding selenium compounds.
5. Describe the commercial process of obtaining each of the following substances, and write equations for the reactions involved in each preparation: chlorine, bromine, sodium hypochlorite, phosphorus, antimony, primary calcium phosphate.
6. Write the following oxidation-reduction reactions; indicate the oxidizing agent and the reducing agent; tell what may be observed when each occurs:
 - (1) nitric acid with hydrochloric acid
 - (2) sulphuric acid with hydrogen bromide
 - (3) sulphuric acid with hydrogen iodide
 - (4) sodium iodide with chlorine
 - (5) sodium bromide with manganese dioxide and sulphuric acid
 - (6) zinc with hydrochloric acid
 - (7) chlorine with lye
7. Write graphic formulas for: bromic acid, perchloric acid, orthophosphoric acid, metarsenious acid, pyroantimonic acid. What is the acid anhydride of each acid?
8. Write equations for the following reactions, and tell what may be observed when each occurs:
 - (1) calcium chloride with silver nitrate
 - (2) ammonia with hydrogen bromide gas
 - (3) bismuth chloride with water
 - (4) silver nitrate with sodium phosphate
 - (5) magnesium chloride with disodium phosphate and ammonium hydroxide
 - (6) antimonious chloride with water
9. Classify the following as oxidizing agents or reducing agents and explain your answer: hydrogen iodide, chlorine, bromine, hydrogen bromide, nitric acid, sulphuric acid.
10. Write formulas for: carbonic acid, silicic acid, germanic acid, stannic acid, metaboric acid.
11. Explain the terms: isotope, atomic number, deuterium, amphoteric hydroxide, halogen, mottled enamel, bleaching-powder, stibine, Marsh test.
12. Write graphic formulas for: magnesium pyrophosphate, calcium metarsenate, secondary magnesium phosphate, primary potassium antimonite, calcium chlorate.

Chapters XXIV to XXVIII

- For each of the following, correlate a property with the use of the element: rubidium, mercury, magnesium, iron, aluminium, copper, lead, platinum.
- Give the formula for a compound occurring in nature for the following: calcium, sodium, iron, aluminium, magnesium, zinc, silver, manganese, chromium. What metals occur in nature as elements?
- For each of the following, correlate a property with the use of the compound: silver bromide, mercuric sulphide, aluminium sulphate, copper sulphate, sodium bicarbonate, sodium metaphosphate, sodium carbonate, barium sulphate.
- Write equations to illustrate the preparation of:
 - copper nitrate from copper
 - ferric oxide from ferric hydroxide
 - gold chloride from gold
 - silver sulphate from silver
 - iron from ferrous oxide ore
 - zinc from zinc sulphide ore
 - calcium oxide from calcium carbonate
 - magnesium chloride from magnesium carbonate
- Give the formula and color of each of the compounds: potassium chromate, silver phosphate, ferric ferrocyanide, potassium permanganate, chromic sulphate, lead sulphide.
- Write equations for the following reactions and tell what could be observed when they occur:
 - $\text{K}_2\text{Cr}_2\text{O}_7 + \text{SnCl}_2 + \text{HCl} \rightarrow \text{KCl} + \text{SnCl}_4 + \text{CrCl}_3 + ?$
 - $\text{KMnO}_4 + \text{FeSO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{KHSO}_4 + \text{MnSO}_4 + \text{Fe}_2(\text{SO}_4)_3 + ?$
 - $\text{K}_2\text{Cr}_2\text{O}_7 + \text{HCl} \rightarrow \text{KCl} + \text{CrCl}_3 + \text{Cl}_2 + ?$
 - $\text{KMnO}_4 + \text{HCl} \rightarrow \text{KCl} + \text{MnCl}_2 + \text{Cl}_2 + ?$
 - $\text{Al}(\text{OH})_3 + \text{NaOH} \rightarrow$
 - $\text{HgCl}_2 + \text{SnCl}_2 \rightarrow$
 - $\text{FeCl}_2 + \text{HNO}_3 + \text{HCl} \rightarrow$
 - $\text{FeCl}_3 + \text{K}_4\text{FeC}_6\text{N}_6 \rightarrow$
- Write formulas for the following:

cuprous oxide
 cupric oxide
 plumbous hydroxide
 plumbous sulphide
 plumbic hydroxide
 orthoplumbic acid

potassium permanganate
 manganous chloride
 manganous permanganate
 ferric ferrocyanide
 barium chromate
 sodium zincate

sodium orthoplumbate
mercurous nitrate
mercuric nitrate

sodium metaluminate
potassium stannate
stannous sulphide

8. Explain the meaning of the terms: alum, alloy, blue vitriol, Paris green, verdigris, metallurgy, monel metal, photomicrograph, eutectic point, eutectic mixture, transmutation, gamma rays, artificial radioactivity, radium emanation, chromium plate, cast iron, stainless steel, galvanized iron, brass.
9. How many liters of hydrogen sulphide gas will be used in forming precipitates from a solution containing 0.15 g. of copper chloride, 0.18 g. of silver nitrate, and 0.12 g. of lead acetate?
10. How many grams of sodium hydroxide will react completely with a solution containing 1.2 g. of aluminium sulphate, 0.8 g. of magnesium chloride, and 2.2 g. of ammonium chloride?
11. What gas is formed when hydrochloric acid is added to a sulphite, a sulphide, and a carbonate? Describe tests that would identify each of the gases.
12. What is the formula, color, and solubility in acid of the three silver halides?
13. Describe tests that would distinguish between a bromide and an iodide.
14. What is the formula, color, and solubility in acid of barium carbonate, barium sulphate, and barium phosphate?
15. Describe the color of the flame produced by the ions: sodium, potassium, calcium, and barium. How is the color of the potassium flame observed when sodium ions are present?
16. Describe tests for the following: ammonium, nitrate, borate, ferric, and aluminium ions.
17. Give the formula, name, and description of the insoluble compound that serves as a test for the following: calcium, magnesium, ferric, aluminium, phosphate, chloride, and sulphate ions.
18. Name some positive ions for which the following substances would be tested: baking-powder; well-water (or hard water); body tissues and fluids; the weighting materials of textiles; insecticide sprays.
19. Name some negative ions for which the following substances would be tested: washing-powders; well-water (or hard water); food preservatives; body tissues and fluids; baking-powder.
20. What weight of zinc oxide and what volume of sulphur dioxide are formed by the complete oxidation of 80 g. of zinc sulphide?
21. An iron ore contains 60 per cent of ferric oxide. What weight of iron is produced by reducing 2,000 g. of the ore with carbon?
22. Five kilograms of limestone rock, containing 76 per cent of calcium carbonate, are heated. What weight of lime is produced?

Chapters XXIX and XXX

1. A volume of 4.5 liters of a gas collected over water at 18° C. and 742 mm. pressure, weighs 5.42 grams. What is the gram-molecular weight of the gas? The gas contains 80 per cent carbon and 20 per cent hydrogen. What is the weight of carbon and of hydrogen in the gram-molecular weight? Derive the formula for the compound.
2. When 6.2 grams of a hydrocarbon are burned to complete oxidation, 17.05 grams of carbon dioxide and 13.95 grams of water are obtained. Calculate the percentage of carbon and of hydrogen in the compound. Derive the formula for the hydrocarbon.
3. At standard temperature and pressure, how many liters will hold 180 grams of ethane?
4. Write the graphic formulas for propane, propene, propine, propanol, propyl aldehyde, propanoic acid.
5. Write the graphic formulas for butane, butene, butine, butanol, butyl aldehyde, butyric acid.
6. Use graphic formulas to show the addition reactions of propene with bromine.
7. How many liters of hydrogen gas will combine with 25 liters of carbon dioxide in the production of methyl alcohol? The volume of hydrogen obtained (at standard conditions) will fill how many liters at 18° C. and 745 mm. pressure?
8. A sample containing 14 cc. of vinegar required 16.2 c.c. of 0.714N sodium hydroxide to neutralize all the acetic acid present. How many grams of acetic acid per c.c. of vinegar?
9. When 30 grams of calcium carbide react with water, how many liters of acetylene gas will be formed? How many liters of oxygen will be used in burning to complete oxidation, the volume of acetylene obtained?
10. Give formulas for the following:

(1) a soap	(10) an amino acid
(2) a liquid hydrocarbon	(11) glycerol
(3) an unsaturated hydrocarbon	(12) lactic acid
(4) an alcohol	(13) acetic acid
(5) an organic acid	(14) chloroform
(6) an organic halide	(15) stearic acid
(7) an ester	(16) oleic acid
(8) a fat	(17) ethylene
(9) an aldehyde	(18) water gas
11. Write equations to illustrate the following reactions:
 - (1) hydrolysis of a salt
 - (2) hydrolysis of starch; of sucrose
 - (3) preparation of soap by reaction of a fat with lye

- (4) preparation of an ester
- (5) reaction of chlorine with ethane; of chlorine with ethylene
- (6) hydrogenation of triolein
- (7) neutralization of lactic acid with lime-water

Chapters XXXI to XXXV

1. Briefly describe all the possible ways of making carbon dioxide gas. Tell which methods may be used to obtain carbon dioxide for baking purposes.
2. Describe the result obtained by dialysis of a mixture of egg-white, water, and salt (sodium chloride). The water surrounding the sac may be changed several times; what test would be used to determine the length of time necessary for dialysis?
3. What is the result of adding a blue ink (positively charged colloid) to a green ink (negatively charged colloid)?
4. What weight of residue would be present in a cake in which a portion of tartrate baking-powder was used, corresponding to 4.2 g. of sodium bicarbonate?
5. How many grams of soap (sodium stearate) will be required to precipitate the calcium ions in a liter of hard water that contains 0.16 g. of calcium sulphate per 100 c.c. of water?
6. How many c.c. of carbon dioxide gas will be formed from the complete reaction of 12 g. (about three teaspoons) of a phosphate baking-powder when dissolved in a batter? This baking-powder contains 33.4 per cent of primary calcium phosphate. Calculate the volume that the carbon dioxide would occupy at 220° C. and 740 mm. pressure.
7. How many grams of baking-soda will be required to neutralize 200 c.c. of a sample of vinegar that is a 0.66N acetic acid solution?
8. Write formulas and names of ten carbon compounds that could be present in foods.
9. Write formulas and names of eight compounds that are useful in the laundry.
10. Explain the terms: isoelectric point, hydration, peptization, zwitterions, adsorption, leavening agent, temporary hardness of water, mordant, synthetic fiber, synthetic dye, mortar, enamel, porcelain, quartz glass.
11. Write the formulas for the following compounds; tell how each is used in the home: cream of tartar, sodium hexa-metaphosphate, water-glass, sodium aluminium sulphate, Zeolite, borax, sodium stearate, hydrogen peroxide, potassium permanganate, sodium hypochlorite, sodium hydroxide, silicon dioxide.
12. What is the chemical composition of the following fibers: wool, silk, cotton, linen, each type of rayon, and nylon?

APPENDIX

SECTION I

THE METRIC UNITS

LENGTH

10 millimeters (mm.) = 1 centimeter (cm.)

10 centimeters = 1 decimeter (dm.)

10 decimeters = 1 meter (m.)

1,000 meters = 1 kilometer (km.)

VOLUME

1 cubic centimeter (c.c.) is the volume of a cube 1 cm. \times 1 cm. \times 1 cm.

1,000 c.c. = 1 liter (l.)

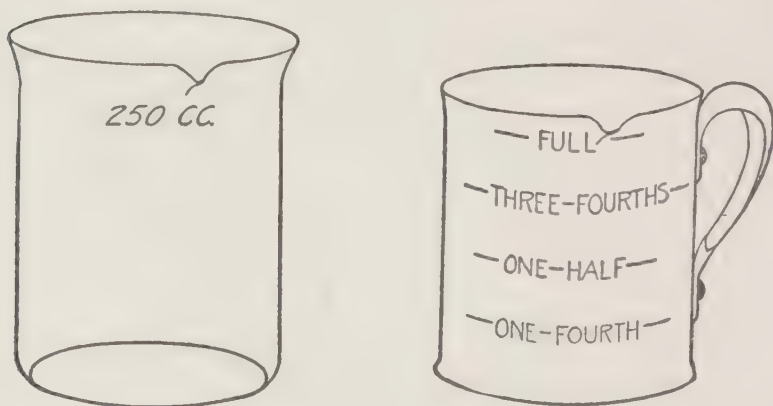


FIG. 45. Comparison of Volumes: Beaker and Measuring Cup

WEIGHT

10 milligrams (mg.) = 1 centigram (cg.)

10 centigrams = 1 decigram (dg.)

10 decigrams = 1 gram (g.)

1,000 grams = 1 kilogram (kg.)

COMPARISON OF METRIC UNITS WITH OTHER UNITS

- 1 centimeter = 0.3937 inch
 1 meter = 39.37 inches
 1 inch = 2.54 centimeters
 1 cubic centimeter = 0.2 teaspoon
 1 liter = 1.057 quarts
 1 quart = 946 cubic centimeters
 1 tablespoon = 15 cubic centimeters
 1 cup = 237 cubic centimeters
 1 kilogram = 2.2 pounds
 1 pound = 453.6 grams

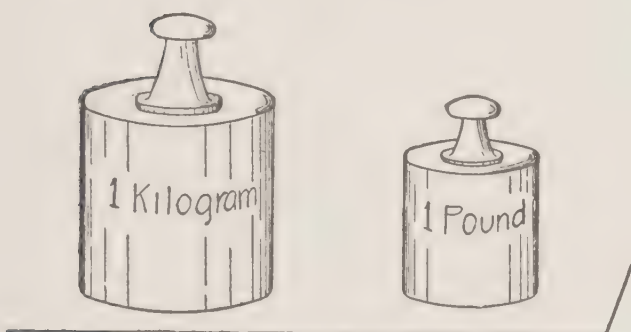


FIG. 46. Comparison of Weights: Kilogram and Pound

SECTION II

WEIGHT IN GRAMS OF ONE LITER OF VARIOUS GASES

(at 0° C. and 760 mm. pressure)

(The weight of one liter of gaseous elements and compounds is determined by the calculation: $\frac{\text{gram-molecular weight.}}{22.4}$.)

<i>Gas</i>	<i>Weight</i>	<i>Gas</i>	<i>Weight</i>
Air	1.293	Hydrogen sulphide	1.521
Ammonia	0.760	Hydrogen chloride	1.627
Carbon dioxide	1.964	Methane	0.716
Chlorine	3.1656	Nitrogen	1.250
Helium	0.1786	Oxygen	1.429
Hydrogen	0.0898	Sulphur dioxide	2.8598

SECTION III

ABSOLUTE HUMIDITY AND TENSION OF AQUEOUS VAPOR

<i>Temperature (C.)</i>	<i>Grams vapor per cubic meter</i>	<i>Tension (pressure) in millimeters of mercury</i>
6	7.3	7.0
10	9.4	9.2
15	12.9	12.8
16	13.6	13.6
17	14.5	14.5
18	15.4	15.5
19	16.3	16.5
20	17.2	17.5
21	18.2	18.6
22	19.4	19.8
23	20.6	21.1
24	21.8	22.4
25	23.1	23.8
26	24.3	25.2
27	25.7	26.7
28	27.2	28.3
29	28.7	30.0
30	30.3	31.8
31	32.0	33.7
32	33.8	35.7

SECTION IV

ELECTROCHEMICAL SERIES

1. Cæsium	14. Cobalt
2. Rubidium	15. Nickel
3. Potassium	16. Tin
4. Sodium	17. Lead
5. Barium	18. Hydrogen
6. Strontium	19. Antimony
7. Calcium	20. Bismuth
8. Magnesium	21. Arsenic
9. Aluminium	22. Copper
10. Manganese	23. Mercury
11. Zinc	24. Silver
12. Chromium	25. Platinum
13. Iron	26. Gold

SECTION V

HYDROGEN ION INDICATORS

<i>Indicator</i>	<i>Color change</i>	<i>pH range</i>
Methyl violet	yellow-blue	0.1- 3.2
Thymol blue	red-yellow	1.2- 2.8
Brom phenol blue	yellow-blue	3.0- 4.6
Methyl orange	red-yellow	3.1- 4.4
Methyl red	red-yellow	4.4- 6.0
Brom cresol purple	yellow-purple	5.2- 6.8
Brom thymol blue	yellow-blue	6.0- 7.6
Phenol red	yellow-red	6.8- 8.4
Cresol red	yellow-red	7.2- 8.8
Thymol blue	yellow-blue	8.0- 9.6
Phenolphthalein	colorless-red	8.3-10.0

SECTION VI

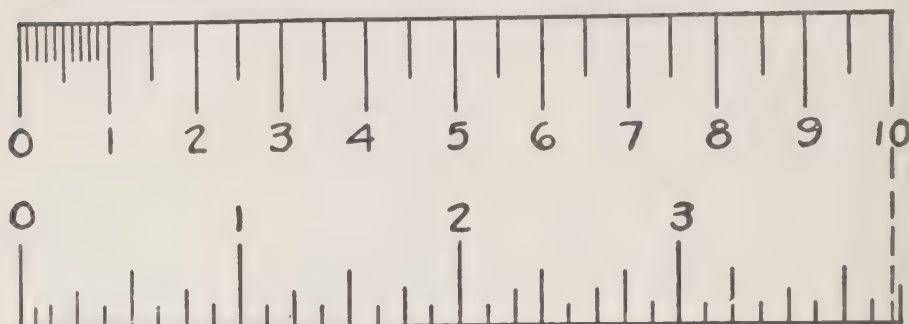
TABLE OF SOLUBILITIES

	K	Na	NH ₄	Ag	Ba	Ca	Mg	Zn	Pb	Al
Cl	s	s	s	i	s	s	s	v s	sl s	s
NO ₃	s	s	s	s	sl s	s	v s	v s	s	v s
OH	s	s	s	—	sl s	sl s	i	i	i	i
SO ₄	s	s	s	sl s	i	sl s	s	s	i	s
CO ₃	s	sl s	s	i	i	i	i	i	i	—
S	s	s	v s	i	—	—	—	i	i	—
PO ₄	s	s	s	i	i	i	i	i	i	i

EXPLANATION: *v s* means more soluble than 100 g. per 100 g. solvent; *s* means between 10 g. and 100 g. per 100 g. solvent; *sl s* means between 0.1 and 10 g. per 100 g. solvent; *i* means less than 0.1 g. per 100 g. solvent.

SECTION VII

COMPARISON OF SCALES, CENTIMETER AND INCH



SECTION VIII

COMPARISON OF CENTIGRADE AND FAHRENHEIT THERMOMETER SCALES

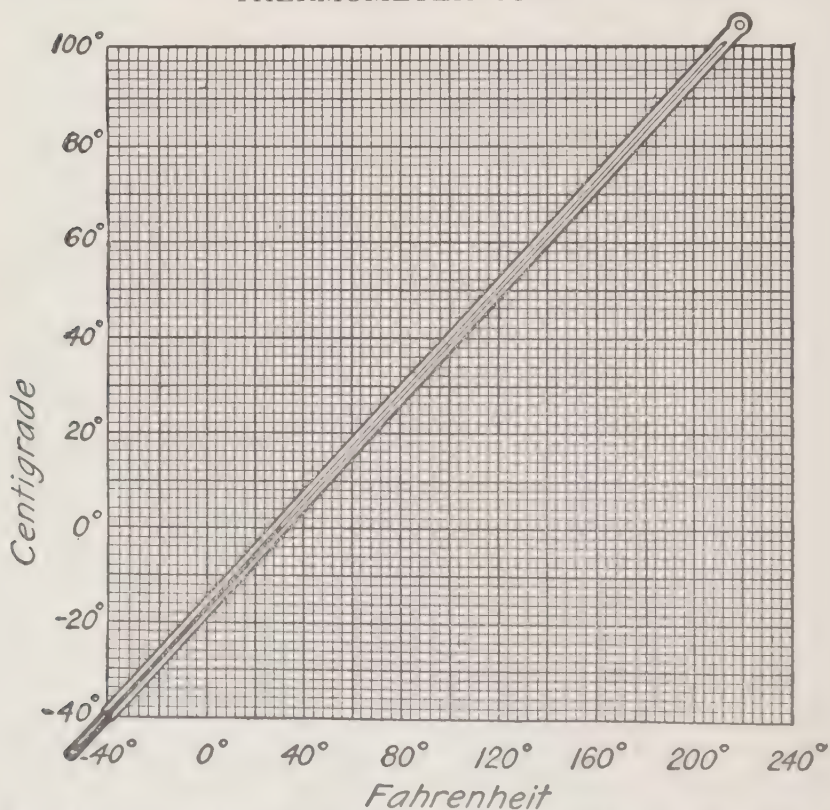


FIG. 47. Temperatures, Centigrade and Fahrenheit (from *At Home among the Atoms* by James Kendall, published by the D. Appleton-Century Company, Inc., 1938).

CORRESPONDING TEMPERATURES—CENTIGRADE AND FAHRENHEIT

	C.	F.
Water Freezes.....	0°	32°
Water Boils.....	100°	212°
$C^{\circ} = \frac{5}{9}(F^{\circ} - 32)$ $F^{\circ} = \frac{9}{5}C^{\circ} + 32$		

Using the diagram, take from the temperature scales the readings that correspond to any point at which the mercury stands in the thermometer.

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NOTE: Unless all references are of equal interest, the bold-face type indicates the references that are most important for an understanding of the topic entry.

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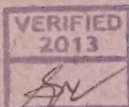
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